12-2010

Soil Chemistry Characterization of Acid Sensitive Watersheds in the Great Smoky Mountains National Park

Mary Ann Elizabeth Grell
mgrell@utk.edu

To the Graduate Council:

I am submitting herewith a thesis written by Mary Ann Elizabeth Grell entitled "Soil Chemistry Characterization of Acid Sensitive Watersheds in the Great Smoky Mountains National Park." I have examined the final electronic copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Environmental Engineering.

John S. Schwartz, Major Professor

We have read this thesis and recommend its acceptance:

Amy M. Johnson, Qiang He

Accepted for the Council:
Carolyn R. Hodges

Vice Provost and Dean of the Graduate School

(Original signatures are on file with official student records.)

To the Graduate Council:

I am submitting herewith a thesis written by Mary Ann Elizabeth Grell entitled "Soil Chemistry Characterization of Acid Sensitive Watersheds in the Great Smoky Mountains National Park." I have examined the final electronic copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Environmental Engineering.

John Schwartz, Major Professor

We have read this thesis
And recommend its acceptance:

Amy Johnson

Qiang He

Accepted for the Council:

Carolyn R. Hodges
Vice Provost and Dean of the Graduate School

(Original signatures are on file with official student records.)

Soil Chemistry Characterization of Acid Sensitive Watersheds in the Great Smoky Mountains National Park

A Thesis Presented for the
Master of Science
Degree
The University of Tennessee, Knoxville

Mary Ann E. Grell
December 2010

Dedication

This thesis is dedicated to the loving memory of my mom, Julia Grell, who always believed in me and taught me how to be strong yet kind.

Acknowledgements

Funding for this research was provided by the National Park Service and the Environmental Protection Agency. I would like to express my sincere gratitude to Dr. John Schwartz, my major professor, for sharing his wealth of knowledge and providing excellent guidance throughout my time in graduate school. I would also like to thank Dr. Amy Johnson and Dr. Qiang He for serving on my thesis committee and contributing to my understanding of soil chemistry. Special thanks to Steve Moore and Matt Kulp from the Great Smoky Mountains National Park for their suggestions and support of my research. I appreciate the members of my research group, especially Dr. Meijun Cai and Keil Neff, who provided helpful input and assisted me on numerous occasions with laboratory work, statistical analyses and GIS work. I am thankful to Doug Klaras, Tim Pobst and Sherman Matthews for their hard work in the field and Galina Malnichenko for performing the total Kjedahl nitrogen measurements.

Abstract

Atmospheric acidic deposition has negatively impacted many Appalachian watersheds in the eastern United States and soils play a key role in the biogeochemical processes that govern the fate and transport of the acidic pollutants. Thus, the collection of soil chemistry data, a previously lacking component, is essential to understand the soil processes related to the retention or release of basic and acidic ions and is imperative for the prediction of ecosystem recovery. Soil chemical properties related to acidification were characterized for 25 sites within eight acid-sensitive watersheds located in the Great Smoky Mountains National Park (GRSM). Relationships were identified by comparing soil chemistry to watershed characteristics including site location, soil characteristics, forest type, geomorphic factors and the presence of Anakeesta. The Walker Camp Prong watershed had significantly higher soil base saturation, calcium and magnesium than all other study watersheds as a result of the application of dolomitic limestone to roadways for wintertime traction control. Significant differences in soil chemistry between the spatially close watersheds of Cosby and Rock Creek demonstrated how local factors can substantially influence the watershed acidification response. The chemical properties of the six study soil types, representing 60% of the entire GRSM, had no significant differences, suggesting soil chemistry must be governed by external inputs and basin characteristics, more so than parent material. This idea was strengthen by the ability to relate many soil chemical properties to forest type and identifying other chemical properties as functions of elevation, slope and soil depth. Also, the presence of unexposed Anakeesta did not seem to have any significant effect on soil chemical properties because all significant differences could be linked to factors unrelated to surficial geology. The majority of the soils of the GRSM study watersheds seem to be experiencing the deleterious effects of long-term exposure to acidic deposition and it could be assumed that soils in many other areas of the park may be enduring the same. The results provide a comparative baseline dataset and important input parameters for biogeochemical modeling. The relationships identified among watershed factors and soil chemical properties can aid in future study designs.

Table of Contents

INTRODUCTION **1**
METHODS **5**
Site Description **5**
Site Selection for Soil Collection **5**
Soil Sample Collection **7**
Determination of Watershed Factors **9**
Laboratory Analysis of Soil **11**
Moisture Content 11
pH 12
Organic Matter Content 12
Total Kjeldahl Nitrogen and Total Organic Nitrogen 12
Exchangeable Base Cations and Aluminum 13
Exchangeable Nitrate, Sulfate, and Ammonium 14
Total Sulfate 14
Exchangeable Acidity, Effective Cation Exchange Capacity, and Total Base Saturation 14
Data Analysis **15**
RESULTS **17**
Characterization of Soil Type Composition in Study Watersheds **17**
Soil Chemistry Characterization **17**
Means Comparison by Horizon 20
PCA Oriented by Watershed 20
Preliminary Means Comparison by Watershed 20
Final Means Comparison by Watershed (WCP omitted) 23
Means Comparison by Soil Type (WCP omitted) 25
Means Comparison by Forest Type (WCP omitted) 25
Means Comparison by Presence of Anakeesta (WCP omitted) 25
Means Comparison by Elevation (WCP omitted) 29
Means Comparison by Slope (WCP omitted) 29

Statistical Analysis Among Geomorphic Factors 29
Correlation Analysis (WCP omitted) 29
Stepwise Regression Models (WCP omitted) 31
DISCUSSION 34
Horizons 34
Walker Camp Prong 35
Rock Creek and Cosby Creek 36
Other Watersheds 38
Soil Type 39
Forest Type 39
Surficial Geology (Anakeesta) 40
Geomorphic Factors 41
SUMMARY 43
LIST OF REFERENCES 46
APPENDIX 53
VITA 70

List of Tables

Table 1. Study sites in the Great Smoky Mountains National Park, USA with corresponding watershed acid sensitivity factors 7

Table 2. Characteristics of the underlying geology of the six study soil types (Thomas & Khiel 2009). 8

Table 3. Selected soil types for each study watershed and the percent area represented. 9

Table 4. Watershed factors of sample sites in GRSM. 10

Table 5. Mean soil chemistry values in the A horizon of GRSM study sites. 18

Table 6. Mean soil chemistry values in the B/C horizon of the GRSM study sites..... 19

Table 7. Mean comparison of the A and B/C soil horizons. Significant differences appear in bold ($p<0.05$) and N=22. Note pH and Ca/Al are unitless; BS, TON and OM are %; all other chemical values are $cmol_c\ kg^{-1}$ dry soil. 21

Table 8. Watershed means separation analysis with WCP included. Significant differences appear in bold ($p<0.05$). Note pH and Ca/Al are unitless; BS, TON and OM are %; all other chemical values are $cmol_c\ kg^{-1}$ dry soil. 22

Table 9. Watershed means separation analysis of A and B/C horizon soil chemistry with WCP omitted. Significant differences appear in bold ($p<0.05$). Note pH and Ca/Al are unitless; BS, TON and OM are %; all other chemical values are $cmol_c\ kg^{-1}$ dry soil. 24

Table 10. Soil type means separation analysis of A and B/C horizon soil chemistry with WCP omitted. Note there are no significant differences ($p<0.05$). pH and Ca/Al are unitless; BS, TON and OM are %; all other chemical values are $cmol_c\ kg^{-1}$ dry soil. 26

Table 11. Forest type means separation analysis of A and B/C horizon soil chemistry with WCP omitted. Significant differences appear in bold ($p<0.05$). Note pH and Ca/Al are unitless; BS, TON and OM are %; all other chemical values are $cmol_c\ kg^{-1}$ dry soil. 27

Table 12. Geomorphic factors and presence of Anakeesta means separation analysis of A and B/C horizon soil chemistry with WCP omitted. Significant differences appear in bold ($p<0.05$). Note pH and Ca/Al are unitless; BS, TON and OM are %; all other chemical values are 28

Table 13. Correlations of soil chemistry and geomorphic factors. WCP omitted. Significant correlations appear in bold. 30

Table 14. Predictive models for soil pH, OM, Ca^{2+}, Al, Ca/Al, EBC, EA and BS. EA and ion concentrations were expressed in $cmol_c\ kg^{-1}$ dry soil, while OM and BS are %. 33

List of Figures

Figure 1. Study watersheds in the GRSM on the Tennessee-North Carolina border, USA. 6

Figure 2. PCA of soil chemistry oriented by study watersheds of the GRSM. 21

INTRODUCTION

Many areas of the Appalachian United States are experiencing delayed water quality and ecosystem recovery from decades of exposure to atmospheric acidic pollution, despite recent reported reductions in electric utilities and heavy manufacturing emissions (Likens et al. 1996; Stoddard et al. 1999; NADP 2006). Soils play a key role in the biogeochemical processes that determine the watershed response to acidic deposition. Within the soil, the depletion of base cations, the biological transformation of nitrogen, and the retention or release of sulfate comprise the major processes governing the export of acidic anions that leads to stream acidification and degradation (Sullivan 2006). It is evident that water quality cannot be linked to atmospheric pollution without first understanding the contributions of soil in the total ecosystem response (Lawrence 2002). Improvements to the chemical composition of the soils, primarily in base status, must precede that of surface water, and only then will aquatic and terrestrial biota have the ability to recover (Driscoll 2001). The changes in the overall watershed processes necessary for a positive response to acidification can be significantly influenced by various basin factors, climate, season, soil characteristics and existing vegetation (Lovett et al. 1997; Deviney et al. 2006; Sullivan et al. 2007). Therefore, in a biologically diverse environment with a complex terrain, such as the Great Smoky Mountains National Park (GRSM) located in eastern Tennessee and western North Carolina, assessment of recovery from long-term acidic deposition proves to be challenging.

Atmospheric pollution in the form sulfur dioxide (SO_2) and nitrogen oxides (NO_x) can travel great distances of more than 500 km (Driscoll 2001). The particulate matter, containing SO_2 and NO_x, can then react with atmospheric water, oxygen and sunlight to produce sulfuric (H_2SO_4) and nitric acid (HNO_3), the constituents of acid rain. These two strong acids have high dissociation constants and readily dissociate in soil water, creating an influx of hydrogen (H^+), sulfate (SO_4^{2-}) and nitrate (NO_3^-) ions. Consequently, the soil pH is lowered on account of the additional H^+ ions, facilitating the dissolution of aluminum compounds found naturally in most mineral soils (Cronan and Schofield 1990). This transformation from organic aluminum compounds into inorganic aluminum, primarily Al^{3+} and $Al(OH)^{2+}$, proves to be highly toxic to

aquatic and terrestrial biota. Furthermore, due to a high affinity for Al^{3+}, the exchange complex of mineral colloids become saturated with acidic cations, displacing the basic cations into soil solution where they are susceptible to leaching (Tomlinson 2003). The chronic base cation leaching that occurs with long-term acidic deposition gradually lowers the ratio of the exchangeable base cation concentration to the effective cation exchange capacity (ECEC). This ratio, known as the percent base saturation (BS), refers to a soil's ability to maintain a chemical charge balance despite inputs of strong acids. And it has been found that forest soils with a BS of less than 15% are more susceptible to increased aluminum mobilization (Ruess 1983; Cronan & Shofield 1990; Sullivan et al. 2008). Soil acidity also increases the potential for SO_4^{2-} adsorption (Nodvin et al. 1986; Ryan et al. 1989), and although at first this may appear somewhat beneficial, it actually plays a major role in the delayed ecosystem recovery (Sullivan et al. 2008). With decreased atmospheric acid loading, as a result of emission reductions, these previously adsorbed SO_4^{2-} ions are slowly released back into soil solution by desorption, where they can be leached into surface waters. Thus, a suppressed BS and low surface water acid neutralizing capacity (ANC) may prevail for decades to come (Stoddard et al. 1999).

The acidification of soils can also occur from naturally occurring processes (Kahl 1992; Lawrence 2002). In fact, studies have shown that biological transformation of nitrogen may actually contribute more to soil and surface water acidification than the anthropogenic impacts of NO_3^- deposition (Koopmans et al. 1995, Cai et al. 2010a). Mineralization is the enzymatic decomposition of organic matter carried out by soil microorganisms. During this process, large organic molecules are broken down until nitrogen is released in the form of ammonium (NH_4^+). Similarly by the actions of microbes, nitrification further transforms NH_4^+ into NO_3^- while simultaneously generating enough H^+ ions to decrease the soil pH. Although both NH_4^+ and NO_3^- are considered important sources of nitrogen for plants, in excessive amounts they can contribute to weak plant structure by causing plant cell overgrowth. Nitrate is also readily leached from the soil, which can result in base cation depletion and degradation of water quality. The oxidation of mineral pyrite (FeS_2) is a natural contributor of SO_4^{2-}. This typically occurs following excavation or landslides, and results in the release of large amounts of sulfuric acid into the environment. Uptake by plants of some nutrients also releases H^+ ions into the soil

(Brady & Weil 2008). When taking up cationic nutrients, plant roots maintain their charge balance by exuding H^+ into the soil solution.

Prior to the industrial age, forest ecosystems were highly sustainable, possessing the ability to flourish on the same sites for thousands of years, as seen in the world's virgin forests, while never depleting important nutrients (Tomlinson 2003). Natural chemical weathering of minerals, nutrient recycling via mineralization of decomposing trees, and some atmospheric deposition supplied base cations that were immediately adsorbed onto the negatively charged soil exchange sites, where they remained stored for future generations of trees (Ulrich and Matzner 1986; Tomlinson 2003). Acidic deposition has altered the natural soil chemistry mechanisms by displacing base cations on the exchange complex with acidic cations. These displaced base cations are then susceptible to leaching as they act as counterions to the SO_4^{2-} and NO_3^- within the soil solution. Unfortunately in this situation, base cation leaching often exceeds replenishment by slow mineral weathering and results in forests having to rely primarily on the recycling of base cations to supply essential nutrients. However, with continued acidic inputs and eventual forest deterioration, even this supply may not suffice the forest growth needs (Likens et al. 1996; Likens et al. 1998).

In an effort to monitor the impact of long-term atmospheric pollution experienced in the GRSM, extensive water quality data has been collected from 1991 until present in the Noland Divide Watershed (NDW), a high elevation watershed in the GRSM that had been subjected to high inputs of acidic deposition. In 2008, Cai et al. conducted an intensive soil characterization study within the NDW, in conjunction with calculating an input-output budget using available water chemistry. Key findings included: NDW is currently behaving as a SO_4^{2-} sink, the export of NO_3^- is governed by biological mechanisms, there exists an extremely low soil base saturation (<7%) and Ca/Al ratio (<0.001), and the composition of soil is being dominated by organic nitrogen, organic carbon and aluminum. The results emphasized the role of soils in biogeochemical processes related to stream acidification and underlined the necessity to collect soil chemistry data if we are to achieve a complete understanding of the watershed acidification response. Given the importance of these findings, a soil characterization of multiple acid-sensitive watersheds would be of benefit in identifying any spatial differences in soil chemistry

related to acidification and would contribute to a more comprehensive insight to the response of the GRSM as a whole to the long-term effects of acidic deposition.

The objectives of this study were: 1) to spatially characterize dominant soil types in eight acid-sensitive watersheds within the GRSM; 2) to characterize soil chemical properties related to acidification of 25 sites located within eight study watersheds; and 3) to identify relationships between soil chemistry and watershed characteristics by comparing soil chemical properties based on site location, soil characteristics, forest type, geomorphic factors and the presence of Anakeesta. Results of this study will give insight to the current soil chemistry status of the GRSM, an Appalachian area that has received some of the highest acidic deposition rates in North America. The data can be used as a baseline for continued monitoring and as a means to compare this region to other areas similarly affected by long-term acid deposition. It will aid in understanding water quality issues and provide important input parameters for biogeochemical modeling that can potentially project future ecosystem conditions and recovery timelines.

METHODS

Site Description

Within the Great Smoky Mountains National Park (GRSM) of Tennessee and North Carolina USA, eight watersheds were chosen for study (Figure 1). Study sites were identical to those eight watersheds initially selected by Neff et al. (2010) using a statistical block design based on watershed acid sensitivity criteria. These criteria were: (1) basin area either less than 10 km^2 or 10-20 km^2; (2) elevation of the sampling sites were either less than or greater than 1000 m; (3) Anakeesta either present in greater than 10% of the total sub-watershed or not present at all. The eight study watersheds included: Newt Prong (NP), Road Prong (RP), Rock Creek (RC), Lost Bottom Creek (LBC), Jakes Creek (JC), Walker Camp Prong (WCP), Cosby Creek (CC) and Palmer Creek (PC) (Table 1).

Site Selection for Soil Collection

The Soil Survey Geographic (SSURGO) database for GRSM, available through the United States Department of Agriculture (USDA) Natural Resources Conservation Service (NRCS), was used to develop a map in ArcGIS 9.3 to spatially characterize soil type composition found in the eight study watersheds (Appendix A1). Six soil types were chosen for this study based on the percent area they represent in each watershed and throughout the park (Appendix A2). These include Breakneck-Pullback complex (BpF), Ditney-Unicoi complex (DtF), Luftee-Anakeesta complex (LrF), Oconaluftee-Guyot-Cataloochie complex (OwF), Soco-Stecoah complex (SoF), and Spivey-Santeetlah complex (SsD). Characteristics of the underlying geology of these study soil types can be found in Table 2. The USDA-NRCS provides an interpretation of the soil symbols used, including soil name, taxonomic classification, slope, and landscape descriptions. A complete listing of the soil type interpretations for the entire GRSM, including the six sampled in this study, can be found in Appendices A3 and A4.

Soil samples were collected from a total of 25 sites within the eight study watersheds. Three soil collection sites, each comprised of one of the six soil types chosen for analysis, were selected per watershed, with the exception of Jakes Creek which had four. The three soil types selected in

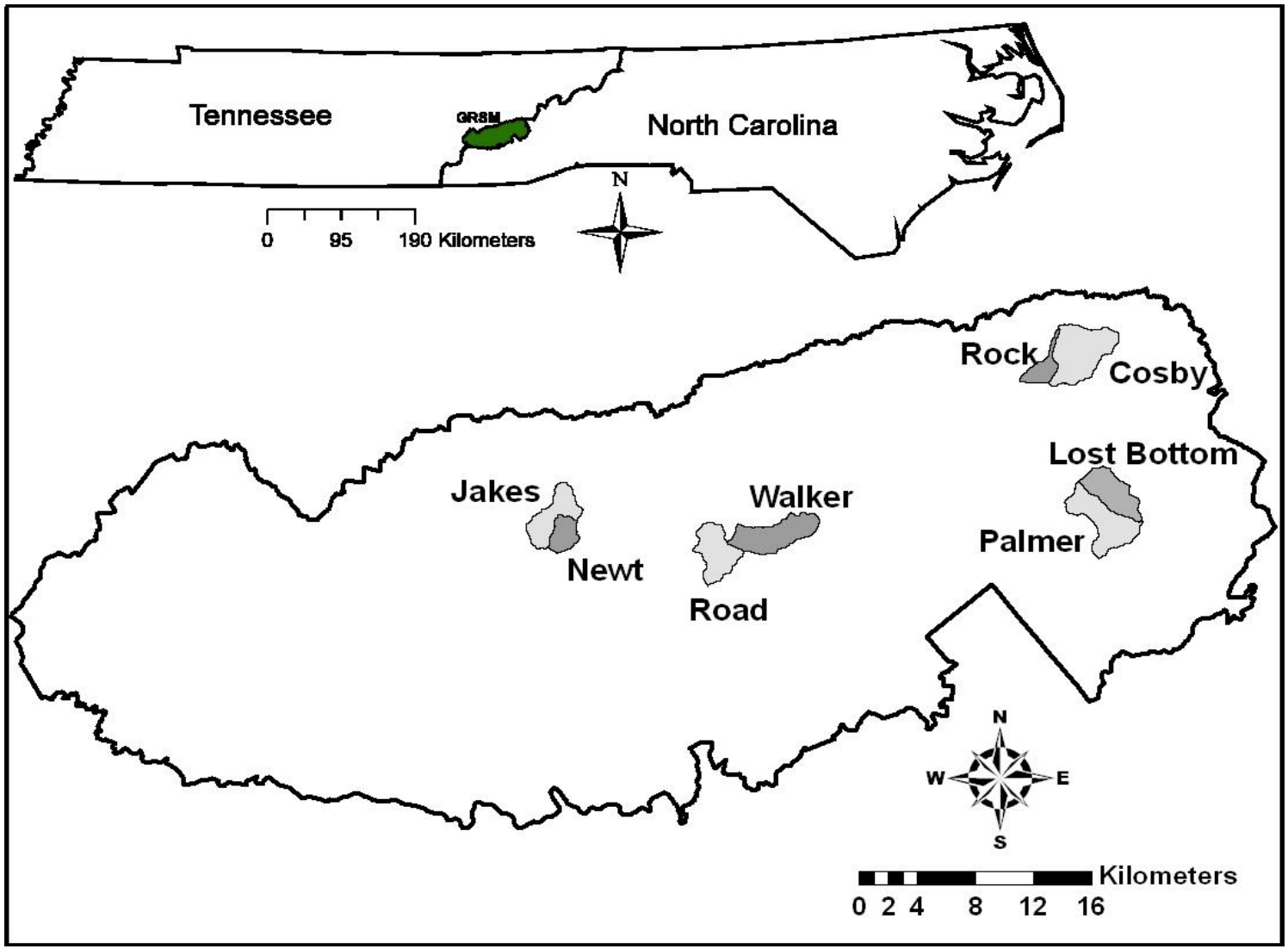


Figure 1. Study watersheds in the GRSM on the Tennessee-North Carolina border, USA.

Table 1. Study sites in the Great Smoky Mountains National Park, USA with corresponding watershed acid sensitivity factors .

Watershed	Basin Area	Elevation	Anakeesta
Newt Prong (NP)	<10 km^2	<1000 m	>10%
Road Prong (RP)	<10 km^2	>1000 m	>10%
Rock Creek (RC)	<10 km^2	<1000 m	None
Lost Bottom Creek (LBC)	<10 km^2	>1000 m	None
Jakes Creek (JC)	10-20 km^2	<1000 m	>10%
Walker Camp Prong (WCP)	10-20 km^2	>1000 m	>10%
Cosby Creek (CC)	10-20 km^2	<1000 m	None
Palmer Creek (PC)	10-20 km^2	>1000 m	None

each watershed were chosen to maximize the percent area of the entire watershed represented by those soils (Table 3). Additional criteria considered that a soil type must be present in at least two of the eight study watersheds and that the site was accessible. Site locations and soil type coverage are illustrated in Appendices A5 through A8.

Soil Sample Collection

Soil samples were collected from October through December 2009. In order to avoid the effect of antecedent precipitation, at least two dry days were required prior to sampling. Because Cai et al. (2010) showed significant differences in soil chemistry between the A horizon and the B horizon but little difference between the B and C horizons, samples were taken from two separate depths, one comprising the A horizon and one the B/C horizon.

At each site, three to five soil cores, from each of the two horizons, totaling 91 excavated soil cores, were taken within close proximity by a random sampling approach. All samples were considered to be disturbed soil, procured using a stainless steel hand auger with a diameter of approximately 8 cm and length of 18 cm. The depth of the A horizon and the total sample depth were measured prior to removing soil from the auger. The depth of core samples taken from the A horizon ranged from 4 to 26 cm, with an average depth of 11 cm. The depth of the

Table 2. Characteristics of the underlying geology of the six study soil types (Thomas & Khiel 2009).

Soil Type	Underlying Geology	Geological Formations	Temperature Regime	Presence of Pyrite Material	Chemical Weathering	Risk of Landslides and/or Stream Acidification	Availability of Plant Macro-nutrients
BpF	Hard Metasandstone	Thunderhead	Frigid	Some embedded black slate	Slow when covered	Moderate risk for both	Very low
DtF	Hard Metasandstone	Thunderhead	Mesic	Some embedded black slate	Slow when covered	Moderate risk for both	Very low
OwF	Soft Metasandstone	Copperhill, Roaring Fork and Elkmont	Frigid	Less sulfur bearing rock than black slate	Moderately rapid	Low risk of landslides and moderate risk for stream acidification	Low
SoF	Soft Metasandstone	Copperhill, Roaring Fork, Elkmont, Wading Branch, Longarm and Wehutty	Mesic	Less sulfur bearing rock than black slate	Moderately rapid	Low risk of landslides and moderate risk for stream acidification	Very low
LrF	Black Slate that can be interbedded with metasandstone	Anakeesta	Frigid	Pyrite-rich black slate	Slow when covered	High risk for both	Very low
SsD	Large basins of colluviums associated with hard metasandstone	Primarily Thunderhead but also Roaring Fork, Elkmont, Wading Branch, Longarm, Pigeon Siltstone and Metcalf Phyllite	Mesic	None	-	No risks	-

Table 3. Selected soil types for each study watershed and the percent area represented.

Study Watershed	Newt	Walker	Rock	Road	Palmer	Lost Bottom	Jakes	Cosby
Soil Type	BpF DtF SsD	BpF DtF LrF	BpF DtF LrF	BpF DtF LrF	DtF SoF OwF	DtF SoF OwF	BpF SoF DtF SsD	BpF DtF SsD
Percent area of study watershed represented by selected soil types	**81.9**	**78.7**	**76.6**	**78.8**	**59.2**	**50.7**	**79.8**	**68.9**

core samples taken from the B/C horizon ranged from 6 to 58 cm, with an average depth of 40 cm. The variation in sample depth was due to the occasional presence of a tree root or rock. All transitional soil was removed from the sample. The soil cores from the same layer were thoroughly combined into an A horizon composite sample and a B/C horizon composite sample for each site. All soil samples were immediately transported to the laboratory and stored in sealed plastic bags at a temperature of 4°C until time of analysis.

Determination of Watershed Factors

Table 4 summarizes the watershed factors for each site including site location, elevation, slope, A horizon depth, total sample depth, soil type, forest type and the presence of the Anakeesta Formation. The coordinates and elevations for each of the sampling locations were measured with a Garmin-Etrex GPS unit. Elevations ranged between 735 m and 1773 m. Sites were assigned to one of two categories, <1000 m or >1000 m. Slopes of each site were obtained by creating a GIS shapefile of the sampling locations to overlay on a DIM. The slopes were then calculated using the DIM. Slopes ranged between 13% and 37%. Sites were assigned to one of two categories, 13-25% moderate slope or 26-37% steep slope.

Likewise using ArcGIS 9.3, the site locations shapefile was used in conjunction with a digital vegetation map created for the GRSM by Madded et al. (2004) to determine dominant forest type for each site (Table 4). Four tree categories were selected as the basis for forest classification in

Table 4. Watershed factors of sample sites in GRSM.

Site ID	West Longitude (degree)	North Latitude (degree)	Mean Elevation (m)	Mean Average Slope (%)	Mean A-Horizon Sample Depth (cm)	Mean Total Sample Depth (cm)	Soil Type	Forest Type	Anakeesta
NP1	83.5876	35.6325	891	24	12	65	SsD	CHx	Absent
NP2	83.5854	35.6324	941	27	14	62	DtF	CHx	Absent
NP3	83.5886	35.6085	1391	24	12	47	BpF	NHx	Present
JC1	83.6072	35.6199	1199	19	15	69	DtF	OzH	Present
JC2	83.6045	35.6120	1421	35	5	45	BpF	CHx	Present
JC3	83.6063	35.6193	1187	13	12	57	SsD	NHx	Present
JC4	83.5830	35.6505	735	17	13	59	SoF	OzH	Absent
WCP1	83.4212	35.6229	1394	14	8	43	LrF	NHx	Present
WCP2	83.4475	35.6259	1214	27	7	54	DtF	NHx	Absent
WCP3	83.4465	35.6265	1287	33	8	58	BpF	NHx	Absent
RP1	83.4706	35.6249	1211	19	10	63	DtF	NHx	Present
RP2	83.4792	35.6237	1389	33	10	62	BpF	NHx	Present
RP3	83.4787	35.6271	1439	20	15	54	LrF	NHx	Present
PC1	83.1507	35.6350	1106	37	11	40	SoF	CHx	Absent
PC2	83.1518	35.6345	1074	29	12	50	DtF	CHx	Absent
PC3	83.1880	35.6417	1440	32	10	59	OwF	CHx	Absent
LBC1	83.1448	35.6376	1067	25	-	-	DtF	OzH	Absent
LBC2	83.1453	35.6372	1048	34	-	-	SsD	CHx	Absent
LBC3	83.1801	35.6665	1680	36	13	40	OwF	S	Absent
RC1	83.2201	35.7260	1561	15	10	24	BpF	NHx	Absent
RC2	83.2379	35.7267	1773	19	13	46	LrF	S	Absent
RC3	83.2199	35.7415	1054	32	6	26	DtF	CHx	Absent
CC1	83.1811	35.7374	1306	27	10	48	BpF	NHx	Absent
CC2	83.1996	35.7480	817	17	12	64	SsD	CHx	Absent
CC3	83.1872	35.7416	1144	31	-	-	DtF	OzH	Absent

this study. Included are the Southern Appalachian Northern Hardwoods (NHx), Southern Appalachian Cove Hardwoods (CHx), Red Spruce (S) and Chestnut Oak/Hardwoods (OzH). The NHx are typically comprised of Northern red oak, black cherry, yellow birch, sugar maple, beech and serviceberry (Whittaker 1956; Madden et al. 2004; Thomas & Khiel 2009). The CHx group may be a mixture of primarily white basswood, silverbell, buckeye, eastern hemlock, yellow poplar and American beech. The OzH includes black oak, scarlet oak, chestnut oak, bitternut hickory, mockernutt hickory, pignut hickory, shortleaf pine, Virginia pine and pitch pine.

Similarly, the presence or absence of Anakeesta at each sample site was determined using the GIS surficial geology layer provided by the GRSM (Table 4). Anakeesta refers to black slate bedrock which is pyrite-rich material (Thomas & Khiel 2009). Chemical weathering of black slate is slow when covered with soil material, but if exposed due to a landslide or excavation, its oxidation can release enormous amounts of sulfate and acidity into the environment. Thunderhead sandstone is sometimes embedded with Anakeesta slate.

Laboratory Analysis of Soil

Soil composite samples were air-dried for 24 to 72 hours at 4°C. Note that after drying soil at this low temperature, samples are not completely dry and still considered wet in lieu of a percentage of water content being lost in the process. Gravel and debris were removed by passing the soil samples through a 2-mm sieve. Only soil with a diameter less than 2-mm was used for chemical analysis and three laboratory replicates were run for all measurements as a quality assurance/quality control measure.

Moisture Content

Moisture content was determined gravimetrically (Hart et al. 1994). Since the composite samples were air-dried at 4°C prior to measurement, these values are not an accurate measure of in-situ moisture content, but rather a means of converting chemical property values into units of kilograms of dry soil. Approximately 5 g of wet soil was placed in an aluminum cup and weighed. The cup containing the soil was then placed in a 105°C oven and allowed to dry to a

constant weight. Moisture content on a dry weight basis was then calculated by subtracting the final dry weight from the initial wet weight.

pH

The soil pH was measured by two methods, water-pH and calcium chloride-pH (Thomas 1996). Approximately 5 g of wet soil was weighed out and placed in a 50 ml plastic centrifuge tube. Either 10 ml of deionized water or 10 ml of 0.01 M $CaCl_2$ was then added to the tube and shaken for 30 minutes in a reciprocate shaker. The slurry was then allowed to stand for 10 minutes and the pH was measured using a pH meter.

Organic Matter Content

The loss-on-ignition (LOI) method was used to determine the soil organic matter content. The organic matter content is assumed to equal the LOI in most surface soils (Nelson & Sommers 1996). Empty aluminum cups were placed in a muffle furnace at 400°C for 2 hours, cooled and weighed to 0.1 mg. Soil was air-dried at room temperature overnight and sieved to a diameter less than 0.4 mm. Approximately 1-3 g of soil was then placed in the cups and heated to 105°C for 24 hr. Upon removing samples from the oven, they were cooled in a dessicator containing $CaCl_2$ and weighed to 0.1 mg. The oven-dried sample weight, W_{105}, could then be calculated by subtracting the weight of the cup. Next the samples were ignited in muffle furnace at 400°C for 16 hr. Afterwards, the cups and the ignited samples were again cooled in a dessicator over $CaCl_2$ and weighted to 0.1 mg. The ignited sample weight, W_{400}, could then be calculated by subtracting the weight of the cup. The organic matter content was then calculated by the following equation,

$$\text{LOI } \% = \frac{W_{105} - W_{400}}{W_{105}} \times 100$$

Total Kjeldahl Nitrogen and Total Organic Nitrogen

The results generated by the Total Kjeldahl Nitrogen (TKN) method are used to calculate the total organic nitrogen (TON) (Bremner 1996). The TKN method consists of a two-step

procedure that involves the digestion of a sample to convert organic N to NH_4^+-N and the determination of NH_4^+-N in the digest. H_2SO_4 is used to promote oxidation of organic matter and conversion of organic N to NH_4^+-N. Catalysts such as Hg, Cu, or Se increase the rate of oxidation of organic matter by H_2SO_4, while K_2SO_4 or Na_2SO_4 increase the temperature of digestion. In a glass digestor tube, a slurry was formed by mixing 0.4 g of wet soil, 1.5 g K_2SO_4, 0.125 g $CuSO_4$ and 3.5 ml concentrated H_2SO_4. A few boiling stones were also added to each tube. The slurry was then dried in a Lachat Instruments Block Digestor BD-46 at 160°C for 2 hours and then digested at 390°C for an additional 2 hours (Hach 2005). Deionized water was added, after the tubes partially cooled, bringing the solution volume to 50 ml. A clear supernate was achieved by allowing the tubes to sit upright in a fume hood for several hours. The concentration of ammonium in the supernate, which actually represents the N-NH_4^+ and organic N which has been reduced to ammonium, known as the TKN concentration, was measured using an Automated Ion Analyzer. Therefore, TKN is equal to the sum of the total organic nitrogen and the ammonium, and once values were determined for the exchangeable ammonium, measured by a different method discussed later, total organic nitrogen was calculated using the equation,

$$\text{TON} = \text{TKN} - \text{Exchangeable } NH_4^+$$

Note the average TKN and average exchangeable NH_4^+ from the three replicates was used in the calculation.

Exchangeable Base Cations and Aluminum

The exchangeable base cations include Ca^{2+}, Mg^{2+}, Na^+ and K^+. For some soil chemical compositions, the use of a specific extractant during the preparation of the sample was necessary. The purpose of the extractant is to extract the chemical of interest off the surface of the soil particles and suspend them in solution for measurement (Sumner & Miller 1996). The extractant used to extract the four base cations and aluminum was a 0.2 M NH_4Cl. Approximately 50 ml of extractant solution was added to 5 g of wet soil in a 50ml centrifuge tube. The slurry was then shaken at 200 rpm for 3 hours in a reciprocating shaker. Next the slurry was centrifuged at 5000

rpm for 10 minutes and filtered through a 0.4 μm membrane. Chemical measurements were taken on the filtrate by inductively coupled plasma spectrometry (ICP).

The calculation of exchangeable aluminum involved an extra step due to aluminum having a species distribution highly dependent on the pH. In order to determine the charge, Phreeqc Interactive 2.13.0 was used to calculate the proportion of aluminum species present based on the soil sample pH. The exchangeable aluminum species includes Al^{+3}, $Al(OH)_2^{+}$ and $Al(OH)^{2+}$.

Exchangeable Nitrate, Sulfate, and Ammonium

The specific extractant used to prepare samples for the measurement of exchangeable nitrate, sulfate, and ammonium is 0.5 mM KCl (Cronan & Schofield 1990; Stams & Marnette 1990). The preparation process is identical to the one for base cations and aluminum. However, chemical measurements are taken on the filtrate using ion chromatography (IC).

Total Sulfate

The specific extractant used to prepare samples for the measurement of total sulfate is 3 mM $Ca(H_2PO_4)_2$ (Tabatabai 1996). The preparation process is identical to the one for exchangeable NO_3^-, SO_4^{2-}, and NH_4^+. Chemical measurements are also taken on the filtrate using ion chromatography (IC).

Exchangeable Acidity, Effective Cation Exchange Capacity, and Total Base Saturation

The exchangeable acidity is the sum of the exchangeable proton and exchangeable aluminum (Sims 1996). It is used in the calculation of the effective cation exchange capacity, which is described later. A direct titration method was used to obtain measurements by adding 5 g of wet soil to 50 ml of 1 M KCl in a plastic 50 ml centrifuge tube. The slurry was then shaken at 200 rpm for 30 minutes in a reciprocating shaker. The tubes were next centrifuged for 10 minutes at 5000 rpm. Following centrifugation, the supernatant was filtered through Buchner funnels using no. 42 Whatman filter paper and 25ml of the filtrate was transferred into a conical flask. A solution of 1 g phenolphthanlein dissolved in 100 ml ethanol was prepared and 3 drops were added to the flask. The filtrate containing the phenolphthanlein was then titrated manually with standardized 0.1 M NaOH until the first permanent pink endpoint was observed. Exchangeable acidity was calculated by the equation,

$$\text{Exchangeable Acidity} = \frac{100MA(x-y)}{W(\text{moisture})}$$

where x is the milliliters of NaOH used for titration , y is the milliliters NaOH used for blank, M is the molarity of NaOH, A is the aliquot factor (A = 2 = 50 ml/25 ml), and W is the weight of wet soil in grams. Resulting units are $cmol_c\ kg^{-1}$ dry soil.

The effective cation exchange capacity (ECEC) is the sum of the exchangeable cations that a soil can adsorb at its native pH (Sumner & Miller 1996; Brady & Weil 2008). The basic cations include Ca^{2+}, Mg^{2+}, Na^{+} and K^{+}, while the acidic cations are H^{+} and Al, collectively known as the exchangeable acidity as mentioned previously. Therefore, the effective cation exchange capacity was calculated by the summation method using the equation,

$$ECEC = Ca^{2+} + Mg^{2+} + Na^{+} + K^{+} + \text{Exchangeable Acidity}$$

Note the average total exchangeable base cations and the average exchangeable acidity from the three replicates were used in the calculation.

The base saturation (BS) gives the percent of the soil exchange sites that are occupied by the base cations (Brady & Weil 2008). Therefore, the base saturation was calculated by dividing the total exchangeable base cations by the effective cation exchange capacity. The total exchangeable base cations is a sum of exchangeable Ca^{2+}, Mg^{2+}, Na^{+} and K^{+} and the average value from the three replicates was used in the calculation.

Data Analysis

A principal component analysis (PCA) was performed on mean values of soil chemical properties as attributes and watersheds as objects generating bi-plots with Euclidean distances as % of maximum based on the correlation matrix (McCune and Grace 2002). In conjunction with the PCA, a multiple means, one-way analysis was used to assess whether significant differences occurred between the mean values of chemical properties among watershed, horizon, soil type,

dominant forest type, elevation, slope and the presence of Anakeesta. Tukey-Kramer HDS was used for means separation and significant differences were based on a p-value less than 0.05. The Pearson correlation method was chosen for the multivariate, pairwise analysis used to identify any relationships between geomorphic factors and soil chemical properties. Predictive models for key chemical parameters were developed using a stepwise regression analysis approach. For the regression analysis, the probability to enter and leave were set at 0.1 with a mixed direction and the dependent variables included pH_{H2O}, organic matter (OM), exchangeable calcium (Ca^{2+}), exchangeable aluminum (Al), total exchangeable base cations (EBC), exchangeable acidity (EA) and base saturation (BS). The PCA analysis was generated using PC-ORD software (McCune and Mefford 1999), while all other statistical computations were performed using JMP 8 software.

RESULTS

Characterization of Soil Type Composition in Study Watersheds

The 39 different soil types that lie in the study watersheds represent 87.6 percent area of all soil types found in the entire GRSM (Appendix A1). Of these soil types, SoF covers the greatest percent area in the GRSM at 29.0 percent and is found in four of the eight study watersheds. The watershed with the most soil types was Palmer Creek, which contained 27 different soil types, while Newt Prong had the least with only 7 soil types. The soil types BpF, DtF and SsE are each present in all of the eight study watersheds, thereby having the greatest frequency of occurrence. The soil type covering the greatest percent area in each study watershed is LrF for Walker Camp Prong at 67.2%, SoF for Palmer Creek at 28.3%, OwF for Lost Bottom Creek at 24.3%, BpF for Rock Creek and Road Prong at 42.5% and 64.4%, respectively, and DtF for Newt Prong, Jakes Creek and Cosby Creek at 44.7%, 43.7% and 34.9%, respectively.

The six soil types chosen for this study represent 60 percent area of the entire GRSM (Appendix A2). For each study watershed, these six soil types were narrowed down to combinations of three or four soil types (Table 3). Newt Prong has the greatest coverage by the selected soil type combination with 81.9% area represented, while Lost Bottom Creek has the least coverage with 50.7% area represented.

Soil Chemistry Characterization

Chemical properties measured and calculated include pH in water (pH_{H20}), pH in calcium chloride (pH_{CaCl2}), organic matter content via loss-on-ignition (OM), total Kjeldahl nitrogen (TKN), total organic nitrogen (TON), exchangeable sodium (Na^+), exchangeable potassium (K^+), exchangeable magnesium (Mg^{2+}), exchangeable calcium (Ca^{2+}), total exchangeable base cations (EBC), exchangeable aluminum (Al), calcium-aluminum ratio (Ca/Al), exchangeable nitrate (NO_3^-), exchangeable ammonium (NH_4^+), exchangeable sulfate (SO_4^{2-}), total sulfate (TSO_4), exchangeable acidity (EA), effective cation exchange capacity (ECEC), and base saturation (BS) (Tables 5 and 6).

Table 5. Mean soil chemistry values in the A horizon of GRSM study sites.

				%			gN kg^{-1} dry soil	$cmol_c$ kg^{-1} dry soil											
Site ID	**pH DI**	**pH $CaCl_2$**	**Ca/Al**	**BS**	**OM**	**TON**	**TKN**	**Na^+**	**K^+**	**Mg^{2+}**	**Ca^{2+}**	**EBC**	**Al**	**NO_3^-**	**NH_4^+**	**SO_4^{2-}**	**TSO_4**	**EA**	**ECEC**
NP1	4.00	3.43	0.15	12.51	21.99	0.53	5.29	0.02	0.40	0.25	0.62	1.30	4.03	0.00	0.04	0.04	0.09	9.06	10.35
NP2	4.11	3.25	0.08	8.94	28.54	0.76	7.56	0.01	0.38	0.37	0.44	1.20	5.37	0.05	0.04	0.02	0.05	12.25	13.45
NP3	3.76	3.50	0.06	7.78	20.72	0.69	6.93	0.02	0.22	0.22	0.26	0.71	4.12	0.46	0.03	0.04	0.18	8.47	9.18
JC1	3.96	3.40	0.07	8.09	20.31	0.49	4.89	0.01	0.35	0.24	0.42	1.02	5.63	0.24	0.07	0.03	0.12	11.75	12.57
JC2	3.91	3.38	0.23	15.58	28.14	0.66	6.61	0.02	0.37	0.54	0.95	1.87	4.14	0.35	0.13	0.07	0.16	9.92	12.03
JC3	4.12	3.67	0.30	18.74	16.86	0.45	4.55	0.01	0.31	0.28	0.90	1.51	3.04	0.30	0.04	0.03	0.09	6.73	8.05
JC4	4.49	3.64	0.02	5.60	12.39	0.26	2.61	0.01	0.20	0.13	0.10	0.44	4.21	0.00	0.11	0.03	0.08	7.47	7.91
WCP1	5.20	4.67	94.88	93.65	20.36	0.51	5.08	0.07	0.16	1.12	7.00	8.34	0.07	0.27	0.04	0.09	0.15	0.57	8.91
WCP2	4.48	3.90	1.00	33.02	9.98	0.30	3.02	0.01	0.24	0.32	1.49	2.05	1.49	0.23	0.02	0.04	0.07	3.97	6.22
WCP3	4.97	4.42	41.81	82.07	11.38	0.35	3.51	0.01	0.21	0.57	4.47	5.26	0.11	0.29	0.03	0.03	0.05	1.15	6.41
RP1	4.37	3.83	1.02	31.71	11.89	0.39	3.89	0.02	0.23	0.40	1.45	2.10	1.42	0.21	0.03	0.03	0.07	4.53	6.63
RP2	4.32	3.65	1.59	31.46	13.74	0.37	3.69	0.02	0.17	0.30	1.68	2.17	1.06	0.25	0.04	0.03	0.06	4.73	6.90
RP3	3.64	3.04	0.61	19.30	48.69	0.90	9.05	0.03	0.32	0.60	2.03	2.98	3.32	0.42	0.05	0.08	0.15	12.45	15.43
PC1	4.24	3.46	1.19	33.57	33.51	0.65	6.54	0.02	0.64	0.82	3.20	4.68	2.68	0.11	0.26	0.09	0.14	9.26	13.94
PC2	3.44	2.69	4.05	34.59	76.17	1.61	16.14	0.04	0.73	1.41	6.17	8.35	1.53	0.32	0.24	0.10	0.10	15.78	24.13
PC3	4.18	3.40	0.20	15.45	24.54	0.64	6.36	0.01	0.62	0.45	0.86	1.94	4.21	0.13	0.09	0.04	0.08	10.59	12.53
LBC1	3.86	2.95	1.31	32.16	54.56	0.97	9.72	0.02	0.84	1.77	3.37	6.00	2.58	0.00	0.19	0.13	0.12	12.66	18.66
LBC2	3.86	2.88	0.94	27.30	56.56	1.15	11.56	0.03	0.84	2.18	2.39	5.44	2.55	0.02	0.19	0.09	0.10	14.50	19.94
LBC3	3.95	3.25	0.05	5.70	32.28	0.71	7.15	0.03	0.29	0.25	0.31	0.89	6.08	0.16	0.13	0.05	0.12	14.66	15.55
RC1	3.39	2.55	0.07	9.08	63.38	1.14	11.44	0.12	0.65	0.68	0.27	1.72	3.90	0.00	0.04	0.08	0.08	17.24	18.96
RC2	3.83	2.92	0.05	5.97	22.19	0.48	4.86	0.02	0.21	0.23	0.22	0.67	4.39	0.02	0.08	0.03	0.05	10.52	11.18
RC3	3.47	2.60	0.31	13.33	78.89	1.18	11.85	0.16	0.57	1.04	0.94	2.71	3.02	0.02	0.13	0.13	0.12	17.59	20.30
CC1	4.01	3.60	0.10	9.52	20.95	0.52	5.23	0.01	0.34	0.17	0.38	0.90	3.74	0.27	0.03	0.04	0.12	8.53	9.43
CC2	5.04	4.30	2.45	44.38	16.71	0.41	4.13	0.01	0.30	0.37	1.92	2.60	0.78	0.07	0.04	0.08	0.37	3.25	5.85
CC3	4.30	3.35	0.26	14.99	28.88	0.68	6.85	0.01	0.51	0.46	1.23	2.21	4.78	0.00	0.19	0.09	0.16	12.56	14.77

Table 6. Mean soil chemistry values in the B/C horizon of the GRSM study sites.

				%			gN kg^{-1} dry soil	$cmol_c$ kg^{-1} dry soil											
Site ID	**pH DI**	**pH $CaCl_2$**	**Ca/Al**	**BS**	**OM**	**TON**	**TKN**	**Na^+**	**K^+**	**Mg^{2+}**	**Ca^{2+}**	**EBC**	**Al**	**NO_3^-**	**NH_4^+**	**SO_4^{2-}**	**TSO_4**	**EA**	**ECEC**
NP1	4.28	3.97	0.03	5.06	6.86	0.15	1.50	0.01	0.09	0.04	0.07	0.22	2.81	0.00	0.01	0.02	0.77	4.23	4.27
NP2	4.52	3.86	0.02	6.34	6.55	0.12	1.25	0.01	0.14	0.06	0.06	0.27	2.49	0.01	0.02	0.01	0.12	4.00	4.27
NP3	4.16	3.99	0.03	6.23	9.83	0.29	2.90	0.02	0.10	0.07	0.07	0.27	2.49	0.11	0.01	0.05	0.84	4.02	4.28
JC1	4.34	3.84	0.02	4.12	9.09	0.17	1.68	0.01	0.11	0.05	0.05	0.22	3.28	0.04	0.04	0.02	0.79	5.08	5.30
JC2	4.19	3.79	0.09	10.20	18.07	0.37	3.70	0.01	0.20	0.16	0.27	0.64	3.15	0.14	0.04	0.04	0.37	5.65	6.30
JC3	4.43	3.92	0.05	7.92	7.73	0.19	1.88	0.01	0.13	0.06	0.14	0.34	2.64	0.08	0.02	0.01	0.60	3.92	4.25
JC4	4.75	4.14	0.01	4.34	3.63	0.06	0.56	0.01	0.07	0.03	0.03	0.15	2.49	0.00	0.01	0.01	0.19	3.26	3.40
WCP1	5.25	4.59	5.85	59.43	9.51	0.26	2.59	0.04	0.05	0.29	1.53	1.92	0.26	0.09	0.01	0.11	0.90	1.12	3.23
WCP2	4.67	4.20	0.32	19.27	5.82	0.17	1.75	0.01	0.08	0.08	0.43	0.60	1.35	0.10	0.01	0.05	0.34	2.72	3.14
WCP3	5.54	4.85	69.88	76.91	7.01	0.26	2.64	0.02	0.13	0.27	3.50	3.92	0.05	0.13	0.01	0.04	0.09	1.18	5.09
RP1	4.67	4.18	0.25	15.74	6.42	0.18	1.75	0.01	0.08	0.10	0.28	0.47	1.13	0.06	0.01	0.02	0.64	2.54	3.02
RP2	4.60	4.01	0.22	12.74	6.51	0.16	1.59	0.01	0.07	0.07	0.29	0.45	1.35	0.07	0.01	0.03	0.32	3.08	3.53
RP3	4.45	4.19	0.11	7.89	13.32	0.19	1.89	0.01	0.05	0.05	0.09	0.21	0.83	0.05	0.01	0.08	1.21	2.45	2.66
PC1	4.83	4.19	0.26	19.24	12.74	0.24	2.45	0.01	0.22	0.17	0.45	0.85	1.71	0.03	0.10	0.09	0.79	3.56	4.41
PC2	3.99	3.53	0.04	3.79	9.46	0.14	1.45	0.01	0.09	0.08	0.21	0.38	5.58	0.04	0.04	0.06	0.20	9.72	10.10
PC3	4.41	3.93	0.01	4.11	7.05	0.13	1.32	0.01	0.10	0.05	0.05	0.20	3.33	0.02	0.03	0.07	0.99	4.73	4.93
LBC1	4.42	3.86	0.03	7.02	9.78	0.12	1.24	0.01	0.21	0.08	0.10	0.40	3.09	0.00	0.05	0.09	0.60	5.33	5.73
LBC2	4.41	3.88	0.01	4.25	7.97	0.11	1.07	0.01	0.15	0.06	0.04	0.26	3.45	0.00	0.03	0.05	0.78	5.93	6.20
LBC3	4.31	3.66	0.01	2.19	7.96	0.15	1.51	0.01	0.07	0.04	0.03	0.16	3.97	0.02	0.06	0.03	0.23	7.20	7.36
RC1	3.78	2.97	0.01	2.01	3.64	0.08	0.79	0.01	0.06	0.03	0.02	0.12	3.38	0.00	0.02	0.02	0.06	5.92	6.04
RC2	4.07	3.32	0.01	1.63	5.12	0.11	1.12	0.01	0.05	0.04	0.04	0.14	5.36	0.01	0.03	0.01	0.04	8.34	8.48
RC3	4.17	3.74	0.01	3.11	16.97	0.19	1.93	0.01	0.17	0.05	0.05	0.27	4.97	0.03	0.06	0.09	0.55	8.44	8.71
CC1	4.35	4.00	0.01	3.55	8.01	0.20	1.97	0.01	0.10	0.04	0.03	0.18	2.98	0.06	0.01	0.05	1.30	4.76	4.93
CC2	4.68	4.23	0.09	10.28	7.14	0.17	1.68	0.00	0.09	0.04	0.15	0.29	1.69	0.01	0.01	0.03	1.31	2.52	2.81
CC3	4.57	3.93	0.04	10.37	12.01	0.25	2.50	0.01	0.29	0.12	0.14	0.57	3.19	0.01	0.04	0.07	0.60	4.90	5.47

Means Comparison by Horizon

All mean values of chemical properties were greater in the A horizon with the exception of pH_{H20}, pH_{CaCl2} and TSO_4 which were greater in the B/C horizon (Table 7). There was a significant difference between the A horizon and the B/C horizon for the mean values of all chemical properties measured except for Al and SO_4^{2-}.

PCA Oriented by Watershed

The PCA for the A horizon explained 82.0% of the variance in the first two axes resulting in unique correlation relations among chemical properties and watersheds. The WCP watershed oriented strongly with pH, NO_3^- Ca^{2+} and EBC eigenvectors (Figure 2). Similarly, RC was oriented alone, but opposite of WCP, and possessed a strong correlation to Al, EA, Na^+ and OM. The remaining watersheds were oriented in pairs, NP with JC, CC with RP, and LBC with PC. Newt Prong and JC were most closely aligned with the Al and TSO_4 eigenvectors, while CC and RP had only a slight difference in orientation and best correlated to TSO_4 and NO_3^-. Lost Bottom Creek and PC were oriented opposite of the four previously mentioned watersheds and were most closely associated with the K^+, NH_4^+, SO_4^{2-} and Mg^{2+} eigenvectors.

The PCA for the B/C horizon explained 77.5% of the variance in the first two axes resulting in unique correlation relations among chemical properties and watersheds. Again, WCP and RC watersheds each oriented similar to their A horizon bi-plots (Figure 2). However, an additional strong relationship between WCP and Mg^{2+} was evident. Rock Creek differed in the B/C horizon with an opposite orientation to the organic matter (LOI) eigenvector and had a strong alignment with the ECEC and NH_4^+ eigenvector instead. Cosby Creek was no longer grouped with RP, but rather oriented on its own with a strong alignment to the TSO_4 eigenvector. Other strong correlations with CC included K^+, TON and organic matter (LOI). Unlike the A horizon, where NP, JC, PC, LBC, and RP were grouped in distinct pairs, these watersheds were oriented relatively close together in the B/C horizon. This indicates that differences between them were likely more subtle in the B/C horizon than in the A horizon.

Preliminary Means Comparison by Watershed

Many of the chemical parameters A soil horizon of WCP had values that were either the highest or the lowest among the study watersheds (Table 8). This included pH_{H20}, pH_{CaCl2}, OM, TON,

Table 7. Mean comparison of the A and B/C soil horizons. Significant differences appear in bold ($p<0.05$) and N=22. Note pH and Ca/Al are unitless; BS, TON and OM are %; all other chemical values are $cmol_c\ kg^{-1}$ dry soil.

Horizon	pH_{H20}	pH_{CaCl2}	Ca/Al	BS	TON	OM	Na^+	K^+	Mg^{2+}	Ca^{2+}	EBC	EA	Al	NO_3^-	SO_4^{2-}	TSO_4	NH_4^+	ECEC
A	**4.01**	**3.31**	**0.69**	**18.44**	**0.71**	**33.27**	**0.03**	**0.43**	**0.60**	**1.37**	**2.43**	**10.66**	3.48	**0.16**	0.06	**0.12**	**0.10**	**13.08**
B/C	**4.38**	**3.87**	**0.06**	**6.92**	**0.17**	**8.90**	**0.01**	**0.12**	**0.07**	**0.12**	**0.32**	**4.98**	2.97	**0.04**	0.04	**0.60**	**0.03**	**5.29**
Prob > F	**<0.01**	**<0.01**	**<0.01**	**<0.01**	**<0.01**	**<0.01**	**0.02**	**<0.01**	**<0.01**	**<0.01**	**<0.01**	**<0.01**	0.22	**<0.01**	0.06	**<0.01**	**<0.01**	**<0.01**

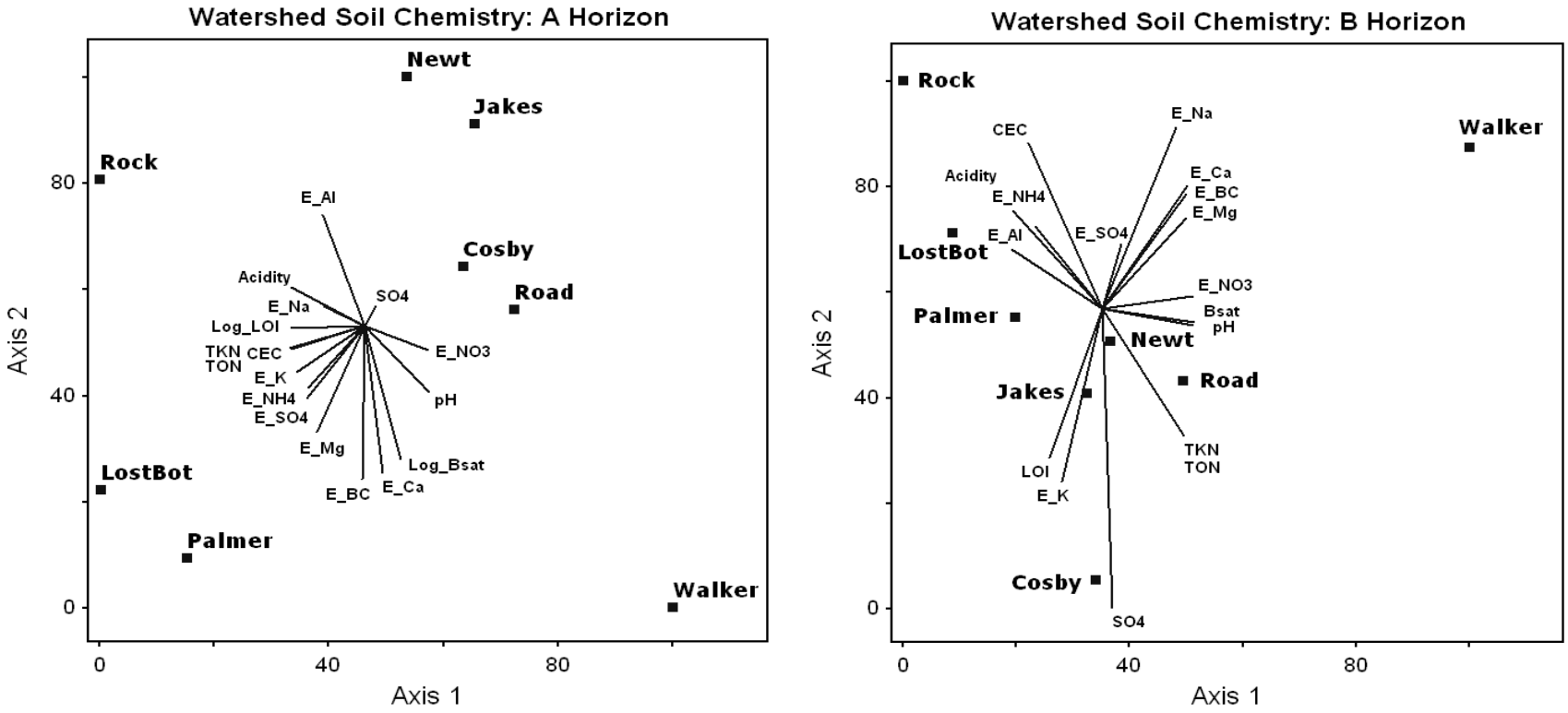


Figure 2. PCA of soil chemistry oriented by study watersheds of the GRSM.

Table 8. Watershed means separation analysis with WCP included. Significant differences appear in bold ($p<0.05$). Note pH and Ca/Al are unitless; BS, TON and OM are %; all other chemical values are $cmol_c\ kg^{-1}$ dry soil.

Horizon	Watershed	WCP	CC	RP	JC	PC	NP	LBC	RC
A	**pH_{H20}**	**4.88 A**	**4.45 AB**	**4.11 AB**	**4.12 AB**	**3.95 AB**	**3.96 AB**	**3.89 B**	**3.57 B**
	pH_{CaCl2}	**4.33 A**	**3.75 AB**	**3.50 ABC**	**3.52 ABC**	**3.18 BC**	**3.39 BC**	**3.03 BC**	**2.69 C**
	Ca/Al	**45.90 A**	**0.94 AB**	**1.07 AB**	**0.16 B**	**1.82 AB**	**0.10 B**	**0.77 AB**	**0.14 B**
	BS	**69.58 A**	**22.96 B**	**27.49 B**	**12.00 B**	**27.87 B**	**9.74 B**	**21.72 B**	**9.46 B**
	TON	0.39 A	0.54 A	0.55 A	0.46 A	0.96 A	0.66 A	0.94 A	0.94 A
	OM	13.91 A	22.18 A	24.78 A	19.42 A	44.74 A	23.75 A	47.80 A	54.82 A
	Na^+	**0.03 AB**	**0.01 B**	**0.02 B**	**0.02 B**	**0.02 AB**	**0.02 B**	**0.03 AB**	**0.10 A**
	K^+	**0.20 B**	**0.38 AB**	**0.24 AB**	**0.31 AB**	**0.66 A**	**0.34 AB**	**0.66 A**	**0.47 AB**
	Mg^{2+}	0.67 A	0.33 A	0.43 A	0.30 A	0.89 A	0.28 A	1.40 A	0.65 A
	Ca^{2+}	4.32 A	1.18 A	1.72 A	0.59 A	3.41 A	0.44 A	2.03 A	0.48 A
	EBC	5.22 A	1.90 A	2.42 A	1.21 A	4.99 A	1.07 A	4.11 A	1.70 A
	EA	**1.90 B**	**8.12 AB**	**7.24 AB**	**8.97 AB**	**11.88 A**	**9.93 AB**	**13.94 A**	**15.12 A**
	Al	**0.56 B**	**3.10 AB**	**1.94 AB**	**4.26 A**	**2.81 AB**	**4.51 A**	**3.74 AB**	**3.77 AB**
	NO_3^-	0.26 A	0.12 A	0.30 A	0.23 A	0.18 A	0.17 A	0.06 A	0.01 A
	SO_4^{2-}	0.05 A	0.07 A	0.04 A	0.04 A	0.08 A	0.04 A	0.09 A	0.08 A
	TSO_4	0.09 A	0.22 A	0.09 A	0.11 A	0.10 A	0.10 A	0.11 A	0.08 A
	NH_4^+	**0.03 B**	**0.09 AB**	**0.04 B**	**0.09 AB**	**0.20 A**	**0.04 B**	**0.17 AB**	**0.08 AB**
	ECEC	7.18 A	10.02 A	9.653 A	10.14 A	16.87 A	11.00 A	18.05 A	16.81 A

Horizon	Watershed	WCP	CC	RP	JC	PC	NP	LBC	RC
B/C	**pH_{H20}**	**5.16 A**	**4.53 AB**	**4.57 AB**	**4.43 B**	**4.41 B**	**4.32 B**	**4.38 B**	**4.01 B**
	pH_{CaCl2}	**4.55 A**	**4.05 AB**	**4.13 AB**	**3.93 BC**	**3.88 BC**	**3.94 ABC**	**3.80 BC**	**3.342C**
	Ca/Al	25.35 A	0.05 A	0.19 A	0.04 A	0.10 A	0.03 A	0.02 A	0.01 A
	BS	**51.87 A**	**8.067 B**	**12.12 B**	**6.65 B**	**9.045 B**	**5.877 B**	**4.487 B**	**2.25 B**
	TON	0.23 A	0.20 A	0.17 A	0.20 A	0.17 A	0.19 A	0.13 A	0.13 A
	OM	7.45 A	9.06 A	8.75 A	9.63 A	9.75 A	7.75 A	8.57 A	8.58 A
	Na^+	0.02 A	0.01 A	0.01 A	0.01 A	0.01 A	0.01 A	0.01 A	0.01 A
	K^+	0.09 A	0.16 A	0.07 A	0.13 A	0.14 A	0.11 A	0.14 A	0.09 A
	Mg^{2+}	**0.218 A**	**0.07 AB**	**0.07 AB**	**0.04 AB**	**0.10 AB**	**0.058 B**	**0.062 B**	**0.04 B**
	Ca^{2+}	**1.82 A**	**0.11 B**	**0.22 B**	**0.12 B**	**0.24 B**	**0.07 B**	**0.06 B**	**0.03 B**
	EBC	**2.15 A**	**0.34 B**	**0.38 B**	**0.34 B**	**0.48 AB**	**0.25 B**	**0.28 B**	**0.18 B**
	EA	**1.67 C**	**4.06 ABC**	**2.60 BC**	**4.48 ABC**	**6.00 AB**	**4.08 ABC**	**6.16 AB**	**7.57 A**
	Al	**0.56 C**	**2.62 ABC**	**1.10 BC**	**2.89 AB**	**3.54 AB**	**2.60 ABC**	**3.50 AB**	**4.57 A**
	NO_3^-	0.11 A	0.03 A	0.06 A	0.06 A	0.03 A	0.04 A	0.01 A	0.01 A
	SO_4^{2-}	0.07 A	0.05 A	0.04 A	0.02 A	0.08 A	0.03 A	0.06 A	0.04 A
	TSO_4	0.44 A	1.07 A	0.72 A	0.49 A	0.66 A	0.58 A	0.53 A	0.22 A
	NH_4^+	0.01 A	0.02 A	0.01 A	0.03 A	0.06 A	0.01 A	0.05 A	0.04 A
	ECEC	**3.82 AB**	**4.40 AB**	**3.07 B**	**4.81 AB**	**6.48 AB**	**4.27 AB**	**6.43 AB**	**7.74 A**

K^+, Ca^{2+}, EBC, Al, NH_4^+, EA, ECEC and BS. It had a significantly higher mean pH_{H20} than LBC and RC and had a significantly higher mean BS than all study watersheds. WCP had a significantly lower mean K^+, Al, NH_4^+ and EA than one or more watersheds. In the A horizon of RC, mean chemistry values for pH_{H20}, OM, Na^+, NO_3^-, EA and BS were also found on the extremes. RC had a significantly higher EA than did WCP and significantly higher Na^+ than did CC, RP, JC and NP. It also had a significantly lower pH_{H20} and BS than did WCP.

Similarly in the B/C horizon, the majority of the chemical properties were extreme values in WCP, with the exception of its mean K^+, SO_4^{2-} and ECEC (Table 8). WCP had a significantly higher pH_{H20}, Mg^{2+} and EBC than several watersheds and had significantly higher BS and Ca^{2+} than all study watersheds. There was a significant difference in the concentrations of mean Ca/Al, Al and EA between WCP and RC, where RC had the highest values for these chemical parameters. Furthermore, the B/C horizon chemistry values for RC occurred on the extremes for several other chemistry values, including mean pH_{H20}, Ca/Al, Ca^{2+}, Mg^{2+}, EBC, ECEC and BS. RC was found to be significantly lower than one or more watersheds for pH_{H20}, Ca^{2+}, Mg^{2+} and EBC. It is also worthwhile to note that CC did have the highest mean concentrations of TSO_4 and K^+, however, the values were not significantly higher than any of the other watersheds.

Final Means Comparison by Watershed (WCP omitted)

The significant differences in the WCP watershed soil chemistry were quite unique. After further investigation, it was discovered that the increased Ca^{2+} concentrations were likely linked to the application of dolomitic limestone used to maintain acceptable wintertime road conditions on US-441, which runs through the WCP and is in close proximity to the sampling locations in that watershed. Because this local anthropogenic factor substantially increased Ca^{2+} concentrations in this area of WCP, we did not feel that the values measured were a true representation of the entire watershed, nor would it be helpful in a comparison study of acid sensitive watersheds of the GRSM. Therefore, the rest of the statistical analyses performed only included the seven remaining watersheds of JC, NP, RP, CC, RC, PC and LBC.

Table 9 provides a means comparison by watershed, omitting WCP. The CC watershed had the highest A horizon pH_{CaCl2}, which was significantly higher than the lowest value found in RC. The A horizon's mean Na^+ concentration in RC was also significantly higher than all other

Table 9. Watershed means separation analysis of A and B/C horizon soil chemistry with WCP omitted. Significant differences appear in bold ($p<0.05$). Note pH and Ca/Al are unitless; BS, TON and OM are %; all other chemical values are $cmol_c\ kg^{-1}$ dry soil.

Horizon	Watershed	CC	RP	JC	PC	NP	LBC	RC
A	**pH_{H20}**	4.45	4.11	4.12	3.95	3.96	3.89	3.57
	pH_{CaCl2}	**3.75 A**	**3.50 AB**	**3.52 A**	**3.18 AB**	**3.39 AB**	**3.03 AB**	**2.69 B**
	Ca/Al	0.94	1.07	0.16	1.81	0.10	0.77	0.14
	BS	22.96	27.49	12.00	27.87	9.74	21.72	9.46
	TON	0.54	0.55	0.47	0.97	0.66	0.95	0.94
	OM	22.18	24.77	19.42	44.74	23.75	47.80	54.82
	Na^+	**0.01 B**	**0.02 B**	**0.02 B**	**0.02 B**	**0.02 B**	**0.03 AB**	**0.10 A**
	K^+	0.38	0.24	0.31	0.66	0.33	0.66	0.47
	Mg^{2+}	0.33	0.43	0.30	0.89	0.28	1.40	0.65
	Ca^{2+}	1.18	1.72	0.59	3.41	0.44	2.03	0.48
	EBC	1.90	2.42	1.21	4.99	1.07	4.11	1.70
	EA	8.12	7.24	8.97	11.88	9.93	13.94	15.11
	Al	3.10	1.94	4.26	2.81	4.51	3.74	3.77
	NO_3^-	0.12	0.29	0.23	0.18	0.17	0.06	0.01
	SO_4^{2-}	0.07	0.05	0.04	0.07	0.04	0.09	0.08
	TSO_4	0.22	0.09	0.11	0.11	0.10	0.11	0.08
	NH_4^+	**0.09 AB**	**0.04 B**	**0.089 AB**	**0.20 A**	**0.04 B**	**0.17 AB**	**0.08 AB**
	ECEC	10.02	9.65	10.14	16.87	11.00	18.05	16.81

Horizon	Watershed	CC	RP	JC	PC	NP	LBC	RC
B/C	**pH_{H20}**	4.53	4.57	4.43	4.41	4.32	4.38	4.01
	pH_{CaCl2}	**4.05 A**	**4.13 A**	**3.92 A**	**3.88 AB**	**3.94 A**	**3.80 AB**	**3.34 B**
	Ca/Al	**0.05 AB**	**0.19 A**	**0.04 AB**	**0.10 AB**	**0.03 AB**	**0.02 B**	**0.01 B**
	BS	8.07	12.12	6.65	9.05	5.88	4.49	2.25
	TON	0.20	0.17	0.20	0.17	0.19	0.13	0.13
	OM	9.06	8.75	9.63	9.75	7.75	8.57	8.58
	Na^+	0.01	0.01	0.01	0.01	0.01	0.01	0.01
	K^+	0.16	0.07	0.13	0.13	0.11	0.14	0.09
	Mg^{2+}	0.07	0.07	0.07	0.10	0.06	0.06	0.04
	Ca^{2+}	0.11	0.22	0.12	0.24	0.07	0.06	0.03
	EBC	0.34	0.38	0.34	0.48	0.25	0.28	0.18
	EA	**4.06 AB**	**2.69 B**	**4.48 AB**	**6.00 AB**	**4.08 AB**	**6.16 AB**	**7.56 A**
	Al	**2.62 AB**	**1.10 B**	**2.89 AB**	**3.54 AB**	**2.60 AB**	**3.50 AB**	**4.57 A**
	NO_3^-	0.03	0.06	0.07	0.03	0.04	0.01	0.01
	SO_4^{2-}	0.05	0.04	0.02	0.07	0.03	0.06	0.04
	TSO_4	1.07	0.72	0.49	0.66	0.58	0.53	0.22
	NH_4^+	0.02	0.01	0.03	0.06	0.01	0.05	0.04
	ECEC	**4.40 AB**	**3.07 B**	**4.81 AB**	**6.48 AB**	**4.27 AB**	**6.43 AB**	**7.74 A**

watersheds except LBC, and PC had a significantly higher mean exchangeable NH_4^+ concentration than RP and NP. In the B/C horizon, RP, CC, JC and NP were all significantly higher in mean pH_{CaCl2} than RC. The RP watershed had a significantly higher mean Ca/Al ratio in the B/C horizon than RC and LBC. And RC had a significantly higher mean EA, Al and ECEC than RP.

Means Comparison by Soil Type (WCP omitted)

Based on this analysis, soil type did not seem to govern the soil chemistry in the GRSM (Table 10). No significant differences in mean chemistry values were found among the six soil types in either soil horizon.

Means Comparison by Forest Type (WCP omitted)

There were only two significant differences in mean chemistry values found in relation to forest type (Table 11). In the A horizon, CHx forests were significantly higher than NHx in their mean NH_4^+, with concentrations of 0.13 and 0.04 $cmol_c\ kg^{-1}$ dry soil respectively. The forest type OzH actually had the highest mean NH_4^+ concentration at 0.14 $cmol_c\ kg^{-1}$ dry soil, however, the variance was too high to be considered significantly different. In the B/C horizon, the S forest type had the highest mean Al concentration of 4.66 $cmol_c\ kg^{-1}$dry soil and was significantly higher than the low value of 2.11 $cmol_c\ kg^{-1}$dry soil found in NHx forests.

Means Comparison by Presence of Anakeesta (WCP omitted)

Sites that contained Anakeesta showed a significant difference in their mean K^+ and NO_3^- levels in the A horizon, with p-values of 0.018 and <0.0001 respectively, compared to those sites without Anakeesta (Table 12). Where Anakeesta was present, the mean K^+ was lower at 0.283 $cmol_c\ kg^{-1}$ dry soil and the mean NO_3^- was higher at 0.321 $cmol_c\ kg^{-1}$ dry soil, compared to 0.500 and 0.079 $Cmol_c\ kg^{-1}$ dry soil, respectively, in its absence.

In the B/C horizon, there were also significant differences between the presence and absence of Anakeesta regarding mean TON, Na^+, Al and NO_3^- concentrations, with p-values of 0.023, 0.014, 0.026 and <0.0001, respectively (Table 12). The Al concentration was higher in the absence of Anakeesta at 3.37 $cmol_c\ kg^{-1}$ dry soil, where it was 18.085 $cmol_c\ kg^{-1}$ dry soil in its presence. The remaining three chemical parameters were all higher in its presence with a mean

Table 10. Soil type means separation analysis of A and B/C horizon soil chemistry with WCP omitted. Note there are no significant differences ($p<0.05$). pH and Ca/Al are unitless; BS, TON and OM are %; all other chemical values are $cmol_c\ kg^{-1}$ dry soil.

Horizon	Soil Type	SoF	LrF	SsD	BpF	OwF	DtF
A	pH_{H20}	4.37	3.74	4.26	3.88	4.06	3.93
	pH_{CaCl2}	3.55	2.98	3.57	3.34	3.32	3.15
	Ca/Al	0.61	0.33	0.96	0.41	0.13	1.01
	BS	19.58	12.64	25.73	14.68	10.58	20.54
	TON	0.45	0.69	0.64	0.68	0.67	0.87
	OM	22.95	35.44	28.03	29.39	28.41	42.75
	Na^+	0.02	0.02	0.02	0.04	0.02	0.04
	K^+	0.42	0.26	0.46	0.35	0.46	0.51
	Mg^{2+}	0.48	0.41	0.77	0.38	0.35	0.81
	Ca^{2+}	1.65	1.12	1.46	0.71	0.58	2.00
	EBC	2.56	1.82	2.71	1.48	1.41	3.37
	EA	8.37	11.48	8.39	9.78	12.63	12.45
	Al	3.45	3.86	2.60	3.39	5.15	3.48
	NO_3^-	0.06	0.22	0.10	0.27	0.14	0.12
	SO_4^{2-}	0.06	0.06	0.06	0.05	0.05	0.07
	TSO_4	0.11	0.10	0.16	0.12	0.10	0.11
	NH_4^+	0.19	0.06	0.08	0.05	0.11	0.13
	ECEC	10.93	13.31	11.05	11.30	14.04	15.79

Horizon	Soil Type	SoF	LrF	SsD	BpF	OwF	DtF
B/C	pH_{H20}	4.79	4.26	4.45	4.22	4.36	4.38
	pH_{CaCl2}	4.17	3.76	4.00	3.75	3.80	3.85
	Ca/Al	0.14	0.06	0.05	0.07	0.01	0.06
	BS	11.79	4.76	6.88	6.95	3.15	7.21
	TON	0.15	0.15	0.15	0.22	0.14	0.17
	OM	8.19	9.22	7.43	9.21	7.51	10.04
	Na^+	0.01	0.01	0.01	0.01	0.01	0.01
	K^+	0.14	0.05	0.12	0.11	0.08	0.16
	Mg^{2+}	0.10	0.05	0.05	0.08	0.05	0.08
	Ca^{2+}	0.24	0.07	0.10	0.14	0.04	0.13
	EBC	0.50	0.17	0.28	0.33	0.18	0.37
	EA	3.41	5.39	4.15	4.68	5.96	5.71
	Al	2.10	3.09	2.65	2.67	3.65	3.39
	NO_3^-	0.01	0.03	0.03	0.08	0.02	0.03
	SO_4^{2-}	0.05	0.05	0.03	0.04	0.05	0.05
	TSO_4	0.49	0.62	0.86	0.58	0.61	0.50
	NH_4^+	0.05	0.02	0.02	0.02	0.05	0.04
	ECEC	3.90	5.57	4.38	5.02	6.14	6.08

Table 11. Forest type means separation analysis of A and B/C horizon soil chemistry with WCP omitted. Significant differences appear in bold ($p<0.05$). Note pH and Ca/Al are unitless; BS, TON and OM are %; all other chemical values are $cmol_c\ kg^{-1}$ dry soil.

Horizon	Forest Type	CHx	OzH	NHx	S
A	**pH_{H20}**	4.03	4.15	3.94	3.89
	pH_{CaCl2}	3.27	3.34	3.40	3.09
	Ca/Al	1.07	0.42	0.53	0.05
	BS	22.85	15.21	18.23	5.84
	TON	0.84	0.60	0.64	0.60
	OM	40.56	29.03	28.03	27.24
	Na^+	0.04	0.02	0.03	0.03
	K^+	0.54	0.47	0.32	0.25
	Mg^{2+}	0.82	0.65	0.38	0.24
	Ca^{2+}	1.94	1.28	0.99	0.26
	EBC	3.34	2.42	1.73	0.78
	EA	11.36	11.11	8.95	12.59
	Al	3.15	4.30	2.94	5.23
	NO_3^-	0.12	0.06	0.27	0.09
	SO_4^{2-}	0.07	0.07	0.05	0.04
	TSO_4	0.13	0.12	0.11	0.08
	NH_4^+	**0.13 A**	**0.14 AB**	**0.04 B**	**0.10 AB**
	ECEC	14.72	13.48	10.65	13.37

Horizon	Forest Type	CHx	OzH	NHx	S
B/C	**pH_{H20}**	4.39	4.52	4.35	4.19
	pH_{CaCl2}	3.90	3.94	3.89	3.49
	Ca/Al	0.06	0.03	0.10	0.01
	BS	7.38	6.46	8.01	1.91
	TON	0.181	0.149	0.182	0.131
	OM	10.31	8.63	7.92	6.54
	Na^+	0.009	0.009	0.013	0.011
	K^+	0.14	0.17	0.08	0.06
	Mg^{2+}	0.08	0.07	0.06	0.04
	Ca^{2+}	0.15	0.08	0.13	0.04
	EBC	0.38	0.33	0.29	0.15
	EA	5.42	4.64	3.81	7.77
	Al	**3.24 AB**	**3.01 AB**	**2.11 B**	**4.66 A**
	NO_3^-	0.03	0.01	0.06	0.02
	SO_4^{2-}	0.05	0.05	0.04	0.02
	TSO_4	0.65	0.54	0.71	0.13
	NH_4^+	0.04	0.04	0.01	0.05
	ECEC	5.78	4.98	4.10	7.92

Table 12. Geomorphic factors and presence of Anakeesta means separation analysis of A and B/C horizon soil chemistry with WCP omitted. Significant differences appear in bold ($p<0.05$). Note pH and Ca/Al are unitless; BS, TON and OM are %; all other chemical values are $cmol_c\ kg^{-1}$ dry soil.

		Elevation			**Slope**			**Anakeesta**		
		<1000 m	**>1000 m**	**Prob > F**	**13-25%**	**36-60%**	**Prob > F**	**Absent**	**Present**	**Prob > F**
	No. Obs.	**4**	**18**		**11**	**11**		**15**	**7**	
A	**pH_{H20}**	**4.41**	**3.92**	**0.02**	1.04	3.98	0.71	4.01	4.01	1.00
	pH_{CaCl2}	3.66	3.23	0.07	3.38	3.23	0.40	3.22	3.49	0.16
	Ca/Al	0.68	0.69	0.99	0.56	0.82	0.55	0.75	0.55	0.67
	BS	17.86	18.57	0.91	17.72	19.16	0.78	18.21	18.95	0.89
	TON	0.49	0.76	0.14	0.61	0.81	0.16	0.78	0.56	0.16
	OM	19.91	36.24	0.15	28.16	38.38	0.25	38.10	22.91	0.11
	Na^+	0.01	0.03	0.34	0.03	0.03	0.70	0.04	0.02	0.32
	K^+	0.32	0.46	0.25	0.37	0.50	0.15	**0.50**	**0.28**	**0.02**
	Mg^{2+}	0.28	0.67	0.20	0.47	0.72	0.28	0.70	0.37	0.18
	Ca^{2+}	0.77	1.50	0.37	1.05	1.69	0.31	1.50	1.10	0.56
	EBC	1.38	2.66	0.26	1.91	2.94	0.24	2.74	1.77	0.30
	EA	8.01	11.25	0.14	9.45	11.85	0.16	11.73	8.37	0.06
	Al	3.60	3.46	0.86	3.40	3.56	0.80	3.59	3.25	0.62
	NO_3^-	0.03	0.18	0.07	0.16	0.15	0.92	**0.08**	**0.32**	**<0.01**
	SO_4^{2-}	0.04	0.07	0.20	0.05	0.07	0.29	0.07	0.04	0.08
	TSO_4	0.15	0.11	0.39	0.13	0.11	0.56	0.12	0.12	0.95
	NH_4^+	0.06	0.11	0.22	**0.06**	**0.13**	**0.02**	0.12	0.06	0.06
	ECEC	9.39	13.90	0.11	11.36	14.79	0.11	14.46	10.11	0.06
B/C	**pH_{H20}**	4.56	4.34	0.13	4.37	4.40	0.81	4.37	4.06	0.77
	pH_{CaCl2}	4.05	3.83	0.19	3.87	3.86	0.94	3.81	3.99	0.20
	Ca/Al	0.04	0.07	0.52	0.06	0.07	0.82	0.04	0.11	0.06
	BS	6.50	7.01	0.85	6.55	7.26	0.72	5.82	9.26	0.10
	TON	0.12	0.18	0.15	0.15	0.19	0.25	**0.15**	**0.22**	**0.02**
	OM	6.05	9.54	0.09	7.51	10.30	0.08	8.33	10.14	0.30
	Na^+	0.01	0.01	0.33	0.01	0.01	0.62	**0.01**	**0.01**	**0.01**
	K^+	0.10	0.12	0.46	0.10	0.14	0.06	0.13	0.11	0.53
	Mg^{2+}	0.04	0.07	0.18	0.05	0.08	0.09	0.06	0.08	0.36
	Ca^{2+}	0.08	0.13	0.42	0.10	0.15	0.30	0.10	0.17	0.16
	EBC	0.23	0.34	0.29	0.26	0.38	0.10	0.30	0.37	0.39
	EA	3.50	5.31	0.10	4.33	5.63	0.13	5.52	3.82	0.06
	Al	2.37	3.10	0.30	2.65	3.29	0.24	**3.37**	**2.12**	**0.03**
	NO_3^-	0.01	0.04	0.08	0.03	0.04	0.79	**0.02**	**0.08**	**<0.01**
	SO_4^{2-}	**0.02**	**0.05**	**0.03**	0.03	0.05	0.08	0.05	0.04	0.48
	TSO_4	0.60	0.60	0.97	0.64	0.57	0.67	0.57	0.68	0.53
	NH_4^+	0.01	0.03	0.08	**0.02**	**0.04**	**0.03**	0.04	0.02	0.13
	ECEC	3.69	5.65	0.07	4.58	6.01	0.09	5.81	4.19	0.07

TON of 0.22% in its presence and 0.15% in its absence, a mean Na^+ of 0.013 $cmol_c\ kg^{-1}$ dry soil in its presence and 0.010 $cmol_c\ kg^{-1}$ dry soil in its absence, and a mean NO_3^- of 0.080 $cmol_c\ kg^{-1}$ dry soil in its presence and 0.016 $cmol_c\ kg^{-1}$ dry soil in its absence.

Means Comparison by Elevation (WCP omitted)

The higher elevation sites, those greater than 1000 m, revealed a significantly lower mean pH_{H20} of 3.92 in the A horizon with a p-value of 0.015 (Table 12). The lower elevation sites, those less than 1000 m, had a mean pH_{H20} of 4.41 in the A horizon.

In the B/C horizon, the mean SO_4^{2-} was significantly greater in the higher elevations with a p-value of 0.019 (Table 12). The mean SO_4^{2-} concentration for the high elevation sites was 0.050 $cmol_c\ kg^{-1}$ dry soil, and for the lower elevations 0.016 $cmol_c\ kg^{-1}$ dry soil. No other significant differences were found between the two elevation groups in either soil horizon.

Means Comparison by Slope (WCP omitted)

In regards to slope, only the mean NH_4^+ concentration was significantly higher in both horizons of steeper slopes (26-37%), with p-values of 0.022 and 0.032, respectively for the A and B/C horizons. Moderate slopes (13-25%) had a mean NH_4^+ concentration of 0.065 and 0.020 $cmol_c\ kg^{-1}$ dry soil, respectively for the A and B/C horizon, whereas, steep slopes had a mean values of 0.132 and 0.014 $cmol_c\ kg^{-1}$ dry soil, respectively.

Statistical Analysis Among Geomorphic Factors

Correlation Analysis (WCP omitted)

Overall, the values for the A horizon soil chemistry did not correlate well with the geomorphic factors of elevation, slope and A horizon depth (Table 13). The mean Na^+ concentration negatively correlated to the depth of the A horizon with a Pearson correlation factor of -0.4761 and a significant probability of 0.039. The mean NH_4^+ positively correlated to slope with a Pearson correlation factor of 0.5905 and a significant probability of 0.0038.

The soil chemical parameters in the B/C horizon were found to correlate, in general, with all three geomorphic factors (Table 13). The elevation negatively correlated to both mean pH values and positively correlated to mean Na^+. The correlation factor and significant probability

Table 13. Correlations of soil chemistry and geomorphic factors. WCP omitted. Significant correlations appear in bold.

		A Horizon			B/C Horizon			
		Elevation	**Slope**	**A-Horizon Depth**	**Elevation**	**Slope**	**A-Horizon Depth**	**Total Sample Depth**
pH_{H2O}	Pearson Correlation	-0.4183	-0.1148	0.1314	-0.4954	0.0872	0.1989	0.5486
	Significant Probability	0.0527	0.6108	0.5918	**0.0191**	0.6997	0.4144	**0.015**
	N	22	22	19	22	22	19	19
pH_{CaCl2}	Pearson Correlation	-0.2886	-0.1958	0.1147	-0.5066	0.0816	0.1263	0.5916
	Significant Probability	0.1927	0.3826	0.64	**0.0161**	0.718	0.6063	**0.0076**
	N	22	22	19	22	22	19	19
Ca/Al	Pearson Correlation	-0.3022	0.1006	0.0073	-0.0319	0.1515	-0.1441	0.1789
	Significant Probability	0.1717	0.6559	0.9764	0.8878	0.5009	0.5561	0.4637
	N	22	22	19	22	22	19	19
BS	Pearson Correlation	-0.3561	0.1158	-0.1314	-0.209	0.1803	-0.1735	0.2371
	Significant Probability	0.1038	0.6078	0.5918	0.3505	0.422	0.4775	0.3284
	N	22	22	19	22	22	19	19
OM	Pearson Correlation	-0.003	0.2437	-0.2451	0.0161	0.5036	-0.5016	-0.3375
	Significant Probability	0.9894	0.2745	0.3119	0.9433	**0.0169**	**0.0287**	0.1576
	N	22	22	19	22	22	19	19
TON	Pearson Correlation	0.0255	0.2819	-0.1627	0.1561	0.3621	-0.4765	-0.1319
	Significant Probability	0.9104	0.2038	0.5058	0.4878	0.0977	**0.0392**	0.5905
	N	22	22	19	22	22	19	19
Na	Pearson Correlation	0.1018	0.0359	-0.4761	0.4345	-0.0512	-0.1488	-0.2708
	Significant Probability	0.6523	0.8738	**0.0393**	**0.0433**	0.8211	0.5432	0.2621
	N	22	22	19	22	22	19	19
K	Pearson Correlation	-0.1927	0.3544	-0.2712	-0.2981	0.4697	-0.5019	-0.2008
	Significant Probability	0.3902	0.1056	0.2614	0.1778	**0.0274**	**0.0285**	0.4097
	N	22	22	19	22	22	19	19
Mg	Pearson Correlation	-0.2167	0.3302	-0.3208	-0.0181	0.5108	-0.4217	-0.1138
	Significant Probability	0.3326	0.1333	0.1805	0.9363	**0.0151**	0.0721	0.6428
	N	22	22	19	22	22	19	19
Ca	Pearson Correlation	-0.2649	0.263	-0.0011	-0.0957	0.3234	-0.2932	0.0773
	Significant Probability	0.2336	0.2369	0.9965	0.6718	0.1421	0.2231	0.7531
	N	22	22	19	22	22	19	19
EBC	Pearson Correlation	-0.2667	0.3156	-0.0948	-0.1584	0.4682	-0.4066	-0.0294
	Significant Probability	0.2302	0.1525	0.6996	0.4813	**0.028**	0.084	0.9048
	N	22	22	19	22	22	19	19
Al	Pearson Correlation	0.3024	0.0642	0.2765	0.2077	0.01869	-0.1703	-0.4518
	Significant Probability	0.1714	0.7764	0.2518	0.3537	0.405	0.4857	0.0521
	N	22	22	19	22	22	19	19
NO_3^-	Pearson Correlation	0.3352	-0.0163	0.0277	0.2919	0.087	-0.4059	0.0056
	Significant Probability	0.1273	0.9425	0.9103	0.1875	0.7004	0.0847	0.9819
	N	22	22	19	22	22	19	19

NH_4^+	Pearson Correlation	-0.1816	0.5909	-0.1672	0.0745	0.5957	-0.1824	-0.4867
	Significant Probability	0.4187	**0.0038**	0.494	0.7419	**0.0033**	0.4549	**0.0346**
	N	22	22	19	22	22	19	19
SO_4^{2-}	Pearson Correlation	-0.1406	0.3409	-0.4516	0.0039	0.5376	-0.3184	-0.4074
	Significant Probability	0.5324	0.1205	0.0522	0.9862	**0.0099**	0.1839	0.0834
	N	22	22	19	22	22	19	19
TSO_4	Pearson Correlation	-0.2548	-0.0584	-0.048	-0.1965	-0.0344	0.0571	0.2948
	Significant Probability	0.2525	0.7964	0.8452	0.3808	0.8792	0.8164	0.2206
	N	22	22	19	22	22	19	19
EA	Pearson Correlation	0.2037	0.2889	-0.0644	0.291	0.2914	-0.2241	-0.554
	Significant Probability	0.3631	0.1922	0.7933	0.1888	0.1883	0.3563	**0.0139**
	N	22	22	19	22	22	19	19
ECEC	Pearson Correlation	0.0569	0.3549	-0.0992	0.2846	0.3384	-0.2635	-0.5674
	Significant Probability	0.8014	0.1051	0.6861	0.1993	0.1235	0.2756	**0.0113**
	N	22	22	19	22	22	19	19

were -0.4954 and 0.019 for pH_{H20}, -0.5066 and 0.016 for pH_{CaCl2}, and 0.4345 and 0.043 for Na^+. The slope positively correlated to OM, K^+, Mg^{2+}, EBC, NH_4^+ and SO_4^{2-}. The correlation factor and significant probability was 0.5036 and 0.017 for OM, 0.4697 and 0.027 for K^+, 0.5108 and 0.015 for Mg^{2+}, 0.4682 and 0.028 for EBC, 0.5979 and 0.0033 for NH_4^+, and 0.5376 and 0.010 for SO_4^{2-}. The A horizon depth had a negative correlation with three chemical parameters in the B/C horizon including OM, TON and K^+. The correlation factor and significant probability was -0.5016 and 0.029 for OM, -0.4765 and 0.0398 for TON, and -0.5019 and 0.029 for K^+. Similarly in the B/C horizon, the total sample depth was negatively correlated with four different chemical parameters including NH_4^+, EA and ECEC. The respective correlation factor and significant probability for these correlations were -0.4867 and 0.035 for NH_4^+, -0.5540 and 0.014 for EA, and -0.5674 and 0.011 for ECEC. The pH_{H20} and pH_{CaCl2} positively correlated to total sample depth with a correlation factors of 0.5486 and 0.5916 and significant probabilities of 0.015 and 0.008, respectively. Results from a pairwise correlation (Pearson) analysis of only the chemical parameters can be found in Appendix A9.

Stepwise Regression Models (WCP omitted)

Models were produced utilizing the relationships between geomorphic factors and soil chemistry, including those correlations that exist among the chemical properties themselves. Table 14 provides a summary of the model equations for some key chemical parameters including pH_{H20},

OM, Ca^{2+}, EBC, Al, EA and BS. In the B/C horizon pH_{H2O} and EA were a function of the total sample depth (r^2_{adj}=0.259789 and 0.266127 respectively) and OM was a function of the A horizon depth (r^2_{adj}=0.207592). The Ca/Al ratio could also be predicted in the B/C horizon as a function of pH_{H2O} (r^2_{adj}=0.292949). All p-values were less than 0.02 for these predictive models.

Table 14. Predictive models for soil pH, OM, Ca^{2+}, Al, Ca/Al, EBC, EA and BS. EA and ion concentrations were expressed in $cmol_c\ kg^{-1}$ dry soil, while OM and BS are %.

$\boldsymbol{pH_{H20}\_BC_{HORZ}} = 3.7630144 + 0.0117307 Depth\_Total$ n = 19; $r^2_{adj} = 0.259789$; p = 0.015
$\boldsymbol{OM\_\ BC_{HORZ}} = 17.413815 - 0.766313 Depth\_A$ n = 19; $r^2_{adj} = 0.207592$; p = 0.0287
$\boldsymbol{Ca^{2+}\_\ A_{HORZ}} = 1.812539 - 27.23641 Na^+ - 1.00981 Mg^{2+} + 7.2745347 NH_4^+ + 0.333083 EA - 1.163734 Al$ n = 22; $r^2_{adj} = 0.908805$; p < 0.0001
$\boldsymbol{Ca^{2+}\_\ BC_{HORZ}} = -0.835906 + 0.1887686 pH_{H20} + 0.076261 TKN$ n = 22; $r^2_{adj} = 0.358301$; p = 0.0057
$\boldsymbol{Al\_\ A_{HORZ}} = 1.6958072 + 0.3483343 EA - 26.60944 Na^+ - 0.815452 Ca^{2+}$ n = 22; $r^2_{adj} = 0.868021$; p < 0.0001
$\boldsymbol{Ca/Al\_\ BC_{HORZ}} = -0.720143 + 0.1785342 pH_{H20}$ n = 22; $r^2_{adj} = 0.292949$; p = 0.0055
$\boldsymbol{EBC\_\ A_{HORZ}} = 1.5846219 + 0.2527635 TKN + 13.024206 NH_4^+ - 0.648592 Al$ n = 22; $r^2_{adj} = 0.895279$; p < 0.0001
$\boldsymbol{EA\_\ BC_{HORZ}} = 9.716528 - 0.093076 Depth\_Total$ n = 19; $r^2_{adj} = 0.266127$; p = 0.0139
$\boldsymbol{BS\_\ BC_{HORZ}} = 13.414775 + 96.003115 NH_4^+ - 3.172348 Al$ n = 22; $r^2_{adj} = 0.630648$; p < 0.0001

DISCUSSION

Horizons

There was a significant difference in most of the soil chemical properties between the A and B/C horizons. This emphasizes the importance of sampling horizons separately because soil characteristics vary considerably with depth and the effects of acidic deposition can differ on account of this. All cations, both basic and acidic, decreased in concentration from the A to B/C horizon, however, there was not a significant difference in Al. Because the ECEC of organic matter is typically very high, it has the ability to adsorb more exchangeable cations than most mineral soils. Although both the A and B/C horizons are considered mineral horizons, the A horizon generally contains partially decomposed, or humified, organic matter (Brady & Weil 2008) and the B/C horizon is almost exclusively mineral soil. This is reflected by the greater organic matter (LOI) in the A horizon compared to the B/C horizon in this study. If the organic matter is higher in nitrogen content, there can be an increase in TON, as seen in these results. Another possibility of the higher A horizon base cation concentration is that the A horizon somewhat limits the leaching of Ca^{2+}, a major contributor to the EBC, through a high root activity of vegetative recycling (Lawrence 2002).

Among the two soil horizons, the A horizon had a lower pH. Nitrification is a key contributor to soil acidification and a possible cause of the lower pH present in the A horizon. Along with mineralization, it can also provide reason for the significantly greater NO_3^- and NH_4^+ in the A horizon. Mineralization and nitrification have the tendency to occur in the A horizon because of its relatively higher organic matter content that often contains large supplies of organic nitrogen (Sullivan 2006). Previous work performed in the Noland Divide watershed (NDW), located in the GRSM, concluded that the ratio of net nitrification to net mineralization rates was 66-90% for the A horizon and 43-78% for the B/C. These values within the ranges found by other studies performed in southeastern forests (Cai et al. 2010 a,b; Joslin et al. 1992; Willard et al. 1997).

The lower pH in the A horizon also increases the potential of aluminum solubilization to occur, resulting in the presence of the higher concentrations of Al and H^+ (Cronan and Schofield 1990). It is evident that this is the reason the ECEC is dominated by the acidic cations in both horizons of these eight GRSM watersheds. And because BS is the fraction of EBC to the total ECEC and EA is the sum of the Al and H^+, it is of no surprise that these parameters likewise decreased in concentration from the A to the B/C horizon. Similar patterns in concentrations have been seen in past studies of both northern and southern Appalachian watersheds (Cai et al. 2010a; Sullivan et al. 2006; Fernandez et al. 2003; Lawrence 2001; David & Lawrence 1996).

Interestingly, the TSO_4 was the only chemical parameter found to be significantly higher in the B/C horizon. Two colloid-ion complexes can form on surfaces of mineral soils, inner- and outer-sphere complexes. Exchangeable ions are those that are held loosely on the outer-sphere and can easily be displaced by other ions. Some ions have the potential to adsorb as inner-sphere complexes and can only be displaced by high affinity ions, if at all. Total sulfate is the summation of the exchangeable sulfate and the sulfate adsorbed as inner-sphere complexes. Therefore, in this study, the approximate percentage of the TSO_4 that was adsorbed as inner-sphere complexes was ~48% in the A horizon and ~93% in the B/C horizon. According to the SO_4^{2-} adsorption studies performed on soils of the NDW, lower soil horizons had a greater capacity to adsorb SO_4^{2-} in that watershed too, thus resulting in higher TSO_4 concentration (Cai et al. 2010a).

Walker Camp Prong

Walker Camp Prong had the most significant differences in soil chemical parameters when compared to the other watersheds. The significantly higher BS in both horizons and the significantly higher Ca^{2+} concentration in the B/C horizon indicate that the cation exchange complex is dominated by calcium in this watershed. Because the solubility of aluminum occurs to a lesser degree with an increase in pH, the relatively higher pH in WCP explains the significantly lower concentrations of Al and EA. In general, as BS decreases, inorganic aluminum concentrations in the soil increase, and this has been found to be most pronounced in soils with a BS less than 15% in the B horizon (Cronan & Shofield 1990; Sullivan et al. 2008).

With the exception of WCP, the remaining seven study watersheds all had a BS less than 15% in the B/C horizon.

According to the original block design by Neff (2010), WCP was considered an acid sensitive watershed. So it was quite perplexing to find that WCP possessed a BS of 69.6% in the A horizon, a value approximately three to seven times greater than the other watersheds, and 51.9% in the B/C horizon, which ranged up to twenty-three times greater as found with RC. In addition to that, significantly higher ANC values were likewise occurring in stream chemistry. But where was this base cation supply, particularly Ca^{2+}, coming from? After further investigation and communications with GRSM park officials, we were alerted to the fact that, in the winter, dolomitic limestone is applied to US-441, which is the road nearest to the soil and stream sampling locations. The limestone is then swept off road surfaces in the spring and deposited outside the GRSM. Very likely, the fine powder becomes air born during the sweeping process and disperses over the surrounding area. Dolomite is composed of calcium magnesium carbonate, which also can explain any increased levels of Mg^{2+} in stream and soil samples.

Because all WCP soil samples were taken in relatively close in proximity to US-441, they most likely did not give a true representation of the watershed as a whole and would not provide an accurate comparison to the other acid sensitive watersheds. Therefore, to prevent skewed results on account of this recent anthropogenic caused outlier, we chose to omit WCP from the remaining statistical analyses regarding comparisons by soil type, forest type, presence of Anakeesta and geomorphic factors.

Rock Creek and Cosby Creek

It is important to point out that RC is a smaller sub-watershed within the larger watershed of CC. Despite their close spatial proximity, RC and CC had a tendency to be on opposite extremes when it came to the chemical properties of their soils. Interestingly, RC had the lowest pH of all watersheds, while CC had one of the highest. This may be explained by the fact that two of the RC sites were at some of the highest elevations sampled. They were located on top of the ridge and likely received higher rates of precipitation than the CC sites. It was also noted through visual observation, that there was an unusually large amount of deadfall present. One of the sites actually had quite a bit of deadfall in the surrounding area, while another site had an extremely

thick organic layer of up to 22 cm before reaching the A horizon. In either case, the accumulation of organic matter in an extremely base poor soil can result in increased soil acidification. Organic matter contains numerous surface functional groups and organic acids from which H^+ can dissociate, facilitating base cations leaching (Brady & Weil 2008). This was reflected in RC having the highest OM and the lowest BS in addition to a low pH. CC, on the other hand, was quite contrary to this, whereas the OM was almost half that of RC and the BS was more than double. The pH in CC was also one of the highest. The BS of RC was the lowest of all study watersheds at 9.46% and 2.25% in the A and B/C horizons, respectively. This extremely low BS indicates that forests of this watershed may be at high risk of aluminum toxicity and nutrient deficiencies. The soil Ca/Al ratio is another good indicator of forest health, where forests in soils with a value less than 1.0 have a greater than 50% probability of impaired growth and those with a value less than 0.5 have a greater than 75% probability (Cronan & Gringal 1995; Palmer et al. 2004). CC and RC respectively are both are at risk, although RC is much more.

Another noteworthy observation is the most frequently sampled soil types in the eight watersheds were those that collected RC (DtF, BpF and LrF), however, many of the soil samples taken in RC appeared visually and texturally different in the B/C horizon compared to other samplings from the same soil types. In general, RC soils had a much more prominent color change among the soil layers and possessed a slightly more sandy consistency. A partially weathered bedrock material also existed at somewhat shallow depths in a few locations. In general, sands have a high pollutant leaching potential and a low resistance to changes in pH (Brady & Weil 2008). As a result, the sandier soils may be contributing to decreased SO_4^{2-} adsorption in RC, which is indicated by RC having the lowest TSO_4 concentration in the B/C horizon compared to the other study watersheds. Higher SO_4^{2-} leaching rates concurrently depletes the base cation supply at a quicker rate than in soils with a higher SO_4^{2-} adsorption capacity. This may be another underlying cause of the low soil BS present in RC which has potentially led to aluminum toxicity of the forests indicated by the significantly higher Al concentrations. There is a good chance that the excessive deadfall is the result of these acid deposition effects, although it is likely compounded by the wooly adelgid infestation endured by

many spruce-fir stands in the GRSM (Stehn et al. 2010; Tomlinson 2003). A combination of the above factors offers a very reasonable explanation for the differences found between the spatially close watersheds of CC and RC.

Other Watersheds

It is also interesting to compare the soil chemistry of LBC and PC to that of RC and CC. Although LBC and PC were similar to RC in that they possessed the next lowest pH levels and the next highest OM content, these two watersheds had a BS similar to CC that was two to three times greater than that of RC. So what accounts for these similarities and differences? Overall, like CC, the forests appeared healthier in the LBC and PC watersheds in comparison to RC. LBC was actually one of two study watersheds, RP being the other, that actually had a Ca/Al ratio greater than 1.0 in the A horizon. The increased BS in LBC and PC may be explained by their lower Al concentrations, which decreases the potential of base cations being displaced from the cation exchange complexes. The higher BS may also be a result of base cations, resupplied via nutrient recycling, being adsorbed regularly by the soil in LBC and PC. Whereas in the case of RC, which had the highest Al concentration, the acidic ions almost completely dominated the exchange complex and the stage of forest deterioration has progressed to the point where the recycled base cations are likely in the process of being depleted. The inner-sphere adsorbed sulfate, as seen by the TSO_4 levels in the B/C horizon, is also two to three times greater in LBC and PC, compared to RC. The fact that increased inner-sphere sulfate adsorption can initially help slow the loss of base cations due to leaching and lower Al concentration, can possibly explain why the soils of CC, LBC and PC are not yet as base poor as those of RC. So then why is the pH lower in LBC and PC compared to CC? This may have to do with the transformation of nitrogen. Since LBC and PC have a TON twice that of CC, as well as the highest NH_4^+ concentrations, it could be expected that mineralization and nitrification are the major contributors to the increased H^+ ion concentration in these two watersheds. Whereas in the case of RC, although it also has a high TON, as mentioned previously, the decreased pH is more likely due to increased acidic inputs in these higher elevations sites and the accumulation of OM in their base poor soils. In fact, the low pH of RC may have reached the point at which the microbes involved with nitrogen transformation processes have ceased activity.

Of the remaining watersheds, RP, NP and JC all had similar soil chemistry values, with the exception of RP having a Ca^{2+} concentration that was three times greater than NP and JC, thus elevating the EBC and BS as well. In fact, RP was considerably higher in Ca^{2+} than all other study watersheds except WCP. RP is a watershed adjacent to WCP and US-441 runs through it as well. This leads to the belief that the dolomitic limestone is also contributing to the soil of this watershed, although it appears to be to a lesser degree due to the sampling sites being further from the road.

Even though some soil chemical parameters may not appear significant on an individual basis, collectively they can explain the differences when comparing the acidification response of various watersheds. And although the soil BS and Ca/Al was relatively higher in the A horizon for some of these study watersheds, it is important to realize that all of them are at risk of experiencing the deleterious effects of acidic deposition based on the B/C horizon percentages, with the exception of WCP (Cronan & Gringal 1995; Palmer et al 2004; Sullivan et al. 2008).

Soil Type

No significant differences were found among the six study soil types. This is not that surprising, given that the various geological formations of GRSM, such as black slate and metasandstone, are very often embedded within each other, resulting in soils generated from a combination of parent materials (Thomas & Khiel 2009). The soil series of the study sites actually consist of complexes that are made up of two or more soil series. When the soils map was developed for the GRSM, the soil series comprising these complexes could not be shown separately due to their intricate pattern. What is most interesting about the lack of differences among these soil types is the suggestion that soil chemistry must therefore be governed by external inputs, basin factors, climate, season and existing vegetation, more so than parent material.

Forest Type

The lifecycles of forest vegetation certainly contribute to the chemical makeup of the soil, both collectively and on an individual species basis. Although the intention of this study was not to comprehensively analyze the effects from vegetation, it was necessary to at least include a comparison of the dominating tree stands existing at each of the sites. In some cases, all sites within a watershed were comprised of the same forest type. In these situations, similarities in

soil chemistry could be seen between watershed and forest type, making it difficult to determine what the underlying factor was that contributed to significant differences.

All four forest types had soils associated with them that were fairly poor in fertility, especially in regards to Ca/Al. Overall, CHx appeared to be the least at risk for impaired growth, while S forests were severely at risk. The NH_4^+ concentrations in the A horizon were significantly lower in NHx forests compared to the CHx forests. A possible explanation for this is that due to the increased TON and OM present in the soils of the CHx forests, increased mineralization may be occuring in these forests. This significant difference was also seen among the A horizon of watersheds, where RP, NP and WCP (when included) had significantly lower NH_4^+ than PC. Interestingly, RP and WCP are dominated by NHx and PC is dominated by CHx. Similarly regarding the significant difference of Al in the B/C horizon, Al is highest in RC and LBC, the only two watersheds with sites comprised of S forests, which likewise have significantly higher Al. RP and WCP (when included) had significantly lower levels of Al, consistent with the significantly lower NHx forests that dominate these two watersheds.

Surficial Geology (Anakeesta)

It was important to include a comparison of soil chemical properties in the presence and absence of Anakeesta due to these areas having a high potential to release sulfuric acid into the environment from the oxidation of pyritic material found in black slate. The question has often been raised whether unexposed Anakeesta can have any significant effect on soil and water chemistry. In this study, there were no significant differences in SO_4^{2-} or TSO_4 between sites containing Anakeesta and those that did not, and all of the significant differences that were found could be related to differences in forest type. Of the sites with Anakeesta present, 71% of them also had NHx forests. And of the sites without Anakeesta, the forest composition was 53% CHx, 20% OzH, 13% S and 13% NHx. Both K^+ and Al were lowest in sites with Anakeesta present and NHx forests; likewise, TON, Na^+ and NO_3^- were highest in both situations. The Al could also be related to the elevation as well. The S forest type, which had significantly higher levels of Al than any other forest type, was present at the two highest sampling sites. Although not significantly different, the higher elevation sites had higher Al. Furthermore, there exists a positive correlation, although not a strong one, between Al and elevation. Based on this study, it

does not appear that the mere presence of Anakeesta itself had any significant effects on soil chemical properties because all of the significant differences found can be linked to external factors unrelated to surficial geology.

Geomorphic Factors

The significantly higher amounts of SO_4^{2-} present in those study sites located at higher elevations is consistent with past studies showing that total acidic deposition generally increases with increasing elevations (Shubzda et al. 1995; Lovett et al. 1997; Lovett & Kinsman 1990). Precipitation tends to increase with elevation, but cloud water deposition, which has more highly concentrated droplets than raindrops, can be the dominant form of atmospheric acidic input in high elevations of the mountains. Rates of acidic deposition via cloud water can also vary according to slope orientation, topographic exposure, canopy type and canopy structure (Weathers et al. 1995). As a result of the increased acidic inputs, the pH is lowered, which is evident in the strong negative correlation existing in this study between pH and elevation ($p=0.02$). Furthermore, higher elevations tend to have steeper slopes with shallow, base-poor soils that have little potential to adsorb strong acidic anions (Palmer et al. 2004). And because nitrogen transformation primarily takes place in the A horizon, it was surprising to find NH_4^+ concentrations significantly higher in steeper slopes where the A horizon can be relatively thin, and thus containing less OM and TON than thicker A horizons. Additionally, this unique finding was supported by the relationship that as slope increases, NH_4^+ increases in the A horizon of the study soils. A possible explanation could be vegetation associated with steeper slopes take up less NH_4^+.

Likewise in the B/C horizon, NH_4^+ was significantly higher in steeper slopes. In addition to several other positive correlations between slope and various chemical parameter concentrations, this could be attributed to the fact that infiltration of chemical constituents into the B/C horizon may occur more easily on account of the shallow A horizons associated with steeper slopes. This thought is also confirmed in the negative correlations between these same chemical parameters and the A horizon depth. However, the decrease in NH_4^+ concentration in the B/C horizon with increased total depth is most likely due to greater mineralization occurring primarily in, and closer to, the A horizon. In general, chemical properties in the B/C horizon

tended to correlate with soil layer thickness, more so than the A horizon. In fact, in the B/C horizon, the pH_{H2O} and EA can be calculated as a function of total sample depth and the OM as a function of A horizon depth.

SUMMARY

It is difficult to generalize about the acidification response of watersheds within the GRSM. Individually, they are influenced by many tightly integrated and constantly changing factors due to the park's great biodiversity, complex terrain, massive geological formations and existing microclimates. This study demonstrated how it is often challenging to differentiate the underlying factor which influences a particular soil's chemistry.

Despite the complexity of the ecosystems of the GRSM, some interesting findings were produced from this research. With the exception of WCP, all other study watersheds are at risk of experiencing the deleterious effects of acidic deposition based on their base saturation being <15% and calcium to aluminum ratios being <1.0 in the B/C horizon. Among the study watersheds, Walker Camp Prong had significantly higher values for soil base saturation, calcium and magnesium as a result of the application of dolomitic limestone to roadways for wintertime traction control. The dolomitic limestone can evidently become air born and disperse over a substantially large surrounding area. Currently, the application of dolomitic limestone seems to be positively impacting the adjacent soils and water, but does not make Walker Camp Prong a good candidate for the comparison of acid sensitive watersheds. The significant differences between the spatially close watersheds of Cosby and Rock Creek demonstrated how specific local factors can have very different influences on the watershed acidification response. In general, Rock Creek appears to be experiencing the most adverse effects of long-term exposure to acidic deposition by possessing the lowest pH that may be attributed to its higher elevation sites receiving increased rates of acidic input and compounded by its decreased sulfate adsorption capacity, increased aluminum concentration and accumulation of organic matter from deteriorated forest health. There is a good possibility that nitrogen transformation is a key contributor to the lower pH found in LBC and PC, however, these watersheds could be maintaining a higher base saturation on account of increased sulfate capacity and the recycling of nutrients by potentially healthier forests.

The importance of sampling the separate horizons was also emphasized in this study by the significant differences seen in most chemical properties between the A and B/C horizons. As seen in previous work in the Noland Divide watershed by Cai et al. (2010 a,b), significantly higher concentrations of nitrate and ammonium in the A horizon indicate that mineralization and nitrification are key contributors to a significantly lower pH in that horizon. The chemical properties of the six study soil types, which represent 60% of the entire park area, had no significant differences, suggesting soil chemistry must be governed by external inputs and basin factors, more so than parent material. Again, considering soil base saturation and calcium to aluminum ratios in the B/C horizon, all forest types were at risk for impaired growth and aluminum toxicity. The southern cove hardwoods appeared to be the least at risk, while the red spruce were the most at risk. Interestingly, several significant differences in soil chemical parameters among the various watershed factors could be related to similar patterns seen in the forest type comparison. And as in the case of Rock Creek, it is not only critical to consider forest type, but forest condition as well. This study also showed no increase or significant difference in exchangeable sulfate, nor total sulfate, in sites that contained Anakeesta. This suggested that unexposed Anakeesta did not have any significant effects on soil chemical properties and those significant differences that were found appeared to be unrelated to surficial geology and could be linked to similar patterns found among the different forest types. In regards to geomorphic factors, the higher elevation sites possessed a significantly lower pH and a significantly greater exchangeable sulfate concentration. This is consistent with past studies showing that the total acidic deposition generally increases with increasing elevation due to increased precipitation and cloud water deposition (Shubzda et al. 1995; Lovett et al. 1997; Lovett & Kinsman 1990). Finally, the chemical properties in the B/C horizon had a general tendency to correlate with soil layer thickness, more so than the A horizon. In fact, in the B/C horizon, the pH and exchangeable acidity can be calculated as a function of total sample depth and the organic matter as a function of A horizon depth.

The majority of the soils of the GRSM study watersheds seem to be experiencing the deleterious effects of long-term exposure to acidic deposition and it could be assumed that soils in many other areas of the park may be enduring the same, especially those watersheds containing

chronically, or episodically, acidic streams. In 2009, Neff's research produced similar patterns in water chemistry among the eight study watersheds providing strong evidence of an existing relationship between soil chemistry and water quality. This relationship supports the idea that water quality in the GRSM will not improve until there is a recovery in soil base status. The results of this soil study can be used to link soil and water chemistry data of acid-sensitive watersheds the GRSM, while providing a comparative baseline dataset for monitoring the effects of future changes of acid deposition in the GRSM. Lastly, these findings can be a useful tool in selecting criteria for future soil study designs.

LIST OF REFERENCES

Brady, N.C., & Weil, R.R. (2008) *Nature and Properties of Soils*. MacMillian Co., New York.

Bremner, J.M. (1996) *Nitrogen-Total*. In: Sparks, D.L. (Ed.), Methods of Soil Analysis, Part 3, Chemical Methods. *Soil Science Society of America*, Madison, 1085-1117.

Cai, M., Johnson, A.M., Schwartz, J.S., Moore, S. E. & Kulp, M.A. (2010a). Soil acid-base chemistry of a high elevation watershed in the Great Smoky Mountains National Park affected by long-term acid deposition. *Journal of Environmental Quality*. (In press)

Cai, M., Schwartz, J.S., Robinson, R. B., Moore, S. E. & Kulp, M.A. (2010c). Long-term effects of acidic deposition on water quality in a high elevation Great Smoky Mountains National Park watershed: use of an ion input-output budget. *Water Air Soil Pollution*,209, 143-156.

Cronan, C.S., & Grigal, D.F. (1995). Use of calcium/aluminum ratios as indicators of stress in forest ecosystems. *Journal of Environmental Quality, 24,* 209-226.

Cronan, C.S., & Schofield, C.L. (1990). Relationships between aqueous aluminum and acid deposition in forested watersheds of North America and Northern Europe. *Environmental Science and Technology*, 24, 1100-1105.

David, M.B. & Lawrence, G.B. (1996). Soil and soil solution chemistry under red spruce stands across the northeastern United States. *Soil Science,* 161, 314-328.

Deviney, F. A., Rice, K. C., & Hornberger, G. M. (2006). Time series and recurrence interval models to predict the vulnerability of streams to episodic acidification in Shenandoah National Park, Virginia. *Water Resources Research*, 42, W09405

Driscoll, C.T., Lawrence, G.B., Bulger, A.J., Bulter, T.J., Cronan, C.S., Eagar, C., et al. (2001). Acid deposition in the northeastern United States: sources and inputs, ecosystem effects, and management strategies. *BioScience, 51(3),* 180-197.

Fernandez, I.J., Rustad, L.E., Norton, S.A., Kahl, J.S., & Cosby, B.J. (2003). Experimental acidification causes soil base cation depletion at the Bear Brook Watershed in Maine. *Soil Science Society of America Journal, 67,* 1909–1919

Gobran, G.R., Selim, H.M., Hultberg, H., & Andersson, I. (1998). Sulfate adsorption-desorption in a Swedish forest soil. *Water, Air, and Soil Pollution, 108*, 411-424.

Hach. (2005). *BD-46 Block Digestor, user manual*.

Hart, S.C., Stark, J.M., Davidson, E.A., & Firestone, M.K. (1994). *Nitrogen mineralization, immobilization and nitrification*. In: Weaver, R.W. (Ed.), Methods of Soil Analysis, Part 2, Microbial and Biochemical Properties. Soil Science Society of America, Madison, 985-1018.

Herlihy, A. T., Kaufmann, P. R., Church, M. R., Wigington, P.J., Webb, J. R., & Sale, M. J. (1993). The effects of acidic deposition on streams in the Appalachian Mountain and Piedmont region of the Mid-Atlantic United-States. *Water Resources Research*, 29, 2687–2703.

Joslin, J.D., Kelly, J.M. & Van Miegroet, H. (1992). Soil chemistry and nutrition of North American spruce-fir stands: evidence for recent change. *Journal of Environmental Quality*, 21, 12-30.

Kahl, J. S., Norton, S. A., Haines, T. A., Rochette, E. A., Heath, R. H., & Nodvin, S. C. (1992). Mechanisms of episodic acidification in low-order streams in Maine, USA. *Environmental Pollution*, 78, 37–44, Medline.

King, H.B., Wang, M.K., Zhuang, S.Y., Hwong, J.L., Liu, C.P., & Kang, M.J. (2006). Sorption of sulfate and retention of cations in forest soils of Lien-Hua-Chi watershed in central Taiwan. *Geoderma, 131*, 143-153.

Koopmans, C.J., Lubrecht, W.C. & Tietema, A. (1995). Nitrogen transformations in two nitrogen saturated forest ecosystems subjected to an experimental decrease in nitrogen deposition. *Plant Soil*, 175, 205-218.

Lawrence, G. B. (2002). Persistent episodic acidification of streams linked to acid rain effects on soil. *Atmospheric Environment*, 36, 1589–1598.

Likens, G. E., Driscoll, C.T., & Buso, D.C. (1996). Long-term effects of acid rain: response and recovery of a forest ecosystem. *American Association for the Advancement of Science*, 272, 244-246.

Likens, G. E., Driscoll, C.T., Buso, D.C., Siccama, T.G., Johnson, C.E., Lovett, G.M., Fahey, T.J., Reiners, W.A., Ryan, D.F., Martin, C.W. & Bailey, S.W. (1998). The biogeochemistry of calcium at Hubbard Brook. *Biogeochemistry*, 41, 89-173.

Lovett, G. M., Bowser, J.J., & Edgerton, E.S. (1997). Atmospheric deposition to watersheds in complex terrain. *Hydrological Processes*, 11, 645-654.

Lovett, G. M. & Kinsman, J.D. (1990). Atmospheric pollutant deposition to high-elevation ecosystems. *Atmospheric Environment*, 24A, 2767-2786.

Madden, M., Welch, R., Jordan, T., Jackson, P., Seavy, R. & Seavy, J. (2004). Digital vegetation maps for the Great Smoky Mountains National Park: final report. Center for Remote Sensing and Mapping Science, Department of Geography, University of Georgia

McCune, B. and Mefford, M.J. 1999. *PC-ORD. Multivariate Analysis of Ecological Data*, Version 4, MjM Software Design, Gleneden Beach Oregon, USA.

McCune, B. and Grace, J.B. 2002. *Analysis of Ecological Communities*, MjM Software Design, Gleneden Beach Oregon, USA.

Mitchell, M.J. (2001). Linkages of nitrate losses in watersheds to hydrological processes. *Hydrological Processes, 15,* 3305-3307.

NADP. (2006). "National Atmospheric Deposition Program 2006 annual summary.", Illinois State Water Survey, NADP Data Report 2006-01, Champaign, Illinois.

Neff, K. (2009). Doctoral Research Proposal: *Stream Acidification in the Great Smoky Mountains National Park: Impacts to Native Brook Trout*. Department of Civil and Environmental Engineering, University of Tennessee, Knoxville.

Nelson, D.W., & Sommers, L.E. (1996) *Total carbon ,organic carbon, and organic matter*. In: Sparks, D.L. (Ed.), Methods of Soil Analysis, Part 3, Chemical Methods. *Soil Science Society of America*, Madison, 961-1010.

Nodvin, S.C., Driscoll, C.T., & Likens, G. E. (1986). The effect of pH on sulfate adsorption by a forest soil. *Soil Science, 142(2),* 69-75.

Nodvin, S.C., Van Miegroet, H., Lindberg, S.E., Nicholas, N.S., & Johnson, D.W. (1995). Acidic deposition, ecosystem processes, and nitrogen saturation in a high elevation southern Appalachian watershed. *Water, Air, and Soil Pollution, 85,* 1647-1652.

Palmer, S.M., Driscoll, C.T., & Johnson, C.E. (2004). Long-term trends in soil solution and stream water chemistry at the Hubbard Brook Experimental Forest: relationship with landscape position. *Biogeochemistry, 68,* 51-70.

Ramakrishna, D.M. & Viraraghavan, T. (2005). Environmental impact of chemical deicers- a review. *Water, Air, and Soil Pollution,* 166, 49-63.

Robinson, R.B., Barnett, T.W., Harwell, G. R., Moore, S. E., Kulp, M. A. & Schwartz, J.S. (2008). pH and acid anion time trends in different elevation ranges in the Great Smoky Mountains National Park. *Journal of Environmental Engineering*, 134, in press.

Ryan, P.F., Horngerger, G.M., Cosby, B.J., Galloway, J.N., Webb, J.R. & Rastetter, E.B. (1989). Changes in chemical compostion of stream water in two catchments in the Shenandoah National Park, Virginia, in response to atmospheric deposition of sulfur. *Water Resources Research*,25,10, 2091-2099.

Shubzda, J., Linderberg, S.E., Garten, C.T., & Nodvin, S.C. (1995). Elevational trends in the fluxes of sulphur and nitrogen in throughfall in the Southern Appalachian Mountains, some surprising result. *Water, Air and Soil Pollution, 85,* 2265-2270.

Sims, J.T. (1996) *Lime Requirement*. In: Sparks, D.L. (Ed.), Methods of Soil Analysis, Part 3, Chemical Methods. Soil Science Society of America, Madison, 491-516.

Stams, A.J.M., & Marnette, E.C.L. (1990). Investigation of nitrification in forest soils with soil percolation columns. *Plant and Soil, 125*, 135-141.

Stehn, S.E. (2009). Influence of exogenous disturbances on bryophyte community assemblage and tree regeneration dynamics in southern Appalachian spruce-fir forests. Thesis for Master of Science in Forest Ecology and Management, Michigan Technological University.

Stoddard, J.L., Jeffries, D.S., Lükewille, A., Clair, T.A., Dillon, P.J., Driscoll, C.T., Forsius, M., Johannesseen, M., Kahl, J.S., Kellogg, J.H., Kemp, A., Mannio, J., Monteith, D.T., Murdoch, P.S., Patrick, S., Rebsdorf, A., Skjelkvåle, B.L., Stainton, M.P., Traaen, T., van Dam, H., Webster, K.E., Wieting, J., & Wilander, A. (1999). Regional trends in aquatic recovery from acidification in North America and Europe. *Nature*. 401(7): 575-578.

Sullivan, T. J., Cosby, B. J., Herlihy, A. T., Webb, J. R., Bulger, A. J., Synder, K. U., et al. (2004). Regional model projections of future effects of sulfur and nitrogen deposition on streams in the southern Appalachian Mountains. *Water Resources Research*, 40, W02101.

Sullivan, T. J., Fernandez, I.J., Herlihy, A.T., Driscoll, C.T., McDonnell, T.C., Nowicki, N.A., Snyder, K.U., Sutherland, J.W. (2004). Acid-base characteristics of soils in the Adirondack Mountains, New York. *Soil Science of America Journal*, 70, 141-152.

Sullivan, T. J., Webb, J. R., Synder, K. U., Herlihy, A. T., & Cosby, B. J. (2007). Spatial distribution of acid-sensitive and acid-impacted streams in relation to watershed features in the southern Appalachian Mountains. *Water, Air, and Soil Pollution*, 182, 57–71.

Sullivan, T.J., Cosby, B.J., Webb, J.R., Dennis, R.L., Bulger, A.J., & Deviney Jr, F.A. (2008). Streamwater acid-base chemistry and critical loads of atmospheric sulfur deposition in Shenandoah National Park, Virginia. *Environmental Monitoring and Assessment, 137,* 85-99.

Sumner, M.E., & Miller, W. P. (1996) *Cation exchange capacity and exchange coefficients*. In: Sparks, D.L. (Ed.), Methods of Soil Analysis, Part 3, Chemical Methods. Soil Science Society of America, Madison, 1201–1229.

Tabatabai, M.A. (1996). *Sulfur*. In: Sparks, D.L. (Ed.), Methods of Soil Analysis, Part 3, Chemical Methods. Soil Science Society of America, Madison, 921-960.

Thomas, D. & Khiel, A. (2009) Soil Survey of Great Smoky Mountains National Park, Tennessee and North Carolina. Publication of the USDA and NRCS.

Thomas, G.W. (1996) *Soil pH and soil acidity*. In: Sparks, D.L. (Ed.), Methods of Soil Analysis, Part 3, Chemical Methods. Soil Science Society of America, Madison, 475-490.

Tomlinson, G.H. (2003). Acidic deposition, nutrient leaching and forest growth. *Biogeochemistry,*65, 51-81.

Ulrich, B. & Matzner, E. (1986). Anthropogenic and natural acidification in terrestrial ecosystems. *Experentia,* 42, 344-350.

Weathers, K.C., Lovett, G.M. & Likens, G.E. (1995). Cloud water deposition to a spruce forest edge. *Atmospheric Environment,* 29, 665-672.

Whittaker, R. H. (1956). Vegetation of the Great Smoky Mountains. *Ecological Monographs,*26, 1, 1-80.

Willard, K.W. J., DeWalle, D. R., Edwards, P. J. & Schnabel, R. R. (1997). Indicators of nitrate export from forested watersheds of the mid-Appalachians, United States of America. *Global Biogeochemical Cycles,*11, 4, 649-656.

APPENDIX

A1. Soil types of the eight study watersheds and the respective percent area represented in each watershed and the entire GRSM. Bold values indicate the soil type that covers the largest percent area in each watershed.

Soil Type	GRSM	Newt	Walker	Rock	Road	Palmer	Lost Bottom	Jakes	Cosby
BaE	0.0					0.6			
BpD	0.4	5.2	0.1	0.4	8.5			2.8	0.2
BpF	7.1	34.3	9.2	**42.5**	**64.4**	0.7	1.7	17.6	26.4
BrE	0.2				0.3	0.2	0.4		0.3
BrF	0.1			1.3		0.1			0.5
CcF	3.9				4.0				3.6
ChF	1.6					2.6	0.3		
CmD	0.1					0.6	0.7		
CuD	0.1					0.3			
CuE	0.1					0.2			
DtD	1.2	1.2						5.2	
DtF	14.7	**44.7**	2.3	28.0	2.9	12.5	23.0	**43.7**	**34.9**
HcE	0.6	2.0	3.5			1.7	2.5	0.7	
HrF	0.1				2.6				
JbD	1.3								0.2
JbE	2.5								0.4
LoC	0.4							0.2	
LrD	0.1		0.6		0.5				
LrF	2.5		**67.2**	6.1	11.4				1.8
OcF	2.0					2.7	0.5		
OwC	0.1					0.5	0.8		
OwD	0.6				3.0	2.1	3.3		
OwE	1.1					10.9	17.8		
OwF	2.7					18.4	**24.3**		
RtF	0.5		13.7		0.2				0.1
RxF	0.8			6.4		0.4	0.6		6.1
RZ	0.0					0.1			
SI	0.1		0.3			0.1			
SoD	1.3					0.4		0.2	
SoF	29.0					**28.3**	13.6	4.5	2.8
SpD	0.1					2.1	0.7		
SpF	1.7					2.1	3.6		
SsB	0.2							0.1	
SsC	2.0			8.6				2.3	9.5
SsD	4.1	3.0		2.4		3.4	3.4	14.0	7.6
SsE	4.3	9.7	3.1	4.3	2.0	5.8	2.7	8.8	5.7
WaC	0.0					0.1			
WaD	0.1					0.9			
WaF	0.2					2.2			

A2. The six soil types to be evaluated in the GRSM study watersheds and the percent area represented collectively by these soil types in each watershed and the entire park.

Soil Type	GRSM	Newt	Walker	Rock	Road	Palmer	Lost Bottom	Jakes	Cosby
BpF	7.1	34.3	9.2	42.5	64.4	0.7	1.7	17.6	26.4
DtF	14.7	44.7	2.3	28.0	2.9	12.5	23.0	43.7	34.9
SsD	4.1	3.0		2.4		3.4	3.4	14.0	7.6
LrF	2.5		67.2	6.1	11.4				1.8
SoF	29.0					28.3	13.6	4.5	2.8
OwF	2.7					18.4	24.3		
Percent area of study watershed represented by six selected soil types	**60.0**	**81.9**	**78.7**	**79.0**	**78.8**	**63.3**	**66.0**	**79.8**	**73.4**

A3. Soil Symbol Legend and Landscape Descriptions for GRSM

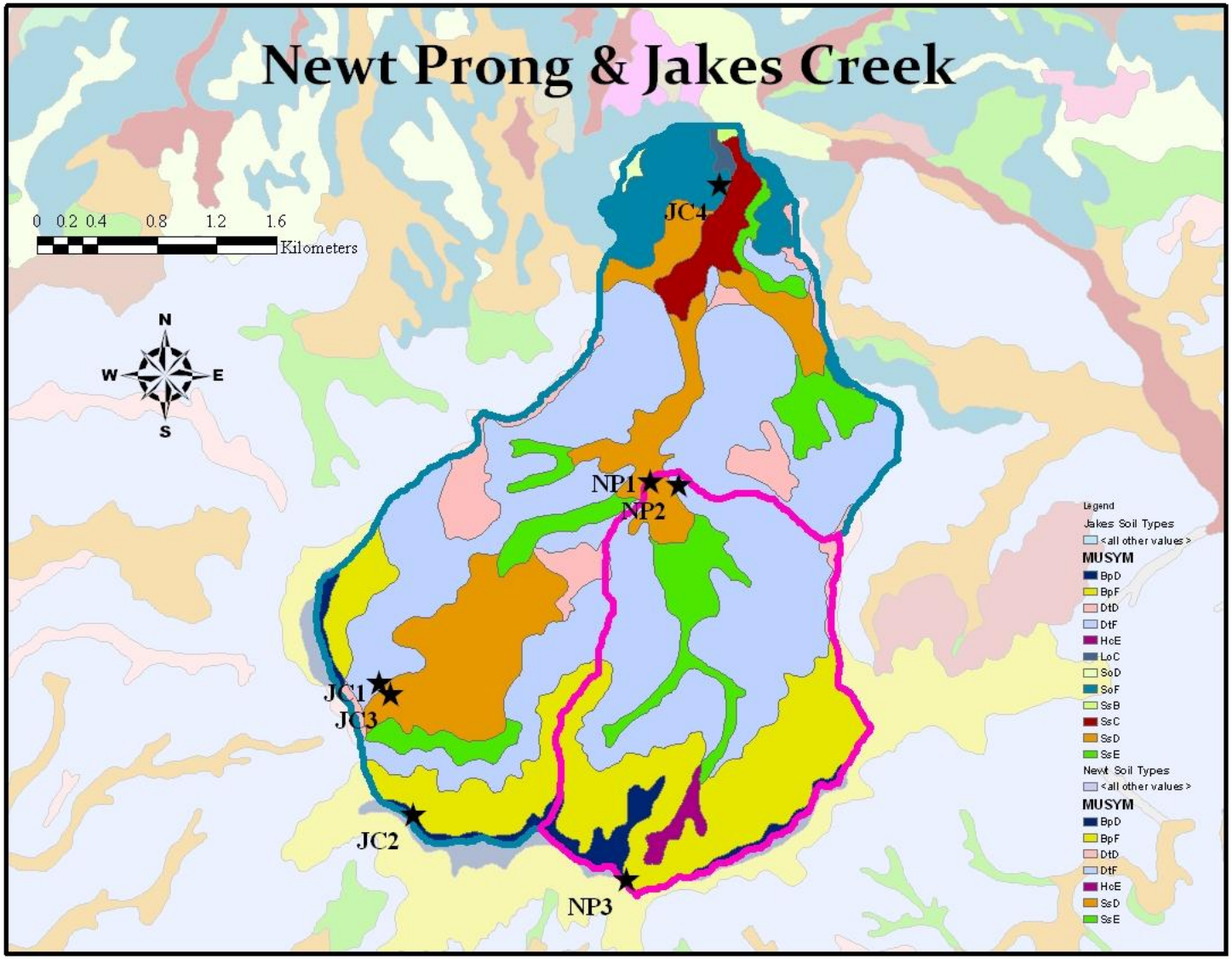
Symbol	Soil Type & Description
AwB	Alarka-Wesser complex, 0 to 8 percent slopes, flooded
AwC	Alarka-Whiteside complex, 8 to 15 percent slopes, stony
AxB	Allegheny loam, 2 to 8 percent slopes
BaE	Balsam-Tanasee complex, 30 to 50 percent slopes, stony
Bm	Biltmore sand, 0 to 3 percent slopes, frequently flooded
BpC	Breakneck-Pullback complex, 8 to 15 percent slopes, very rocky
BpD	Breakneck-Pullback complex, 15 to 30 percent slopes, very rocky
BpF	Breakneck-Pullback complex, 30 to 95 percent slopes, very rocky
BrE	Breakneck-Luftee-Clingman-Pinnacle complex, 15 to 50 percent slopes, very stony
BrF	Breakneck-Luftee-Clingman-Pinnacle complex, 50 to 95 percent slopes, rocky
BuF	Burton-Craggey-Rock outcrop complex, 30 to 95 percent slopes, very stony
CaB	Cades silt loam, 2 to 8 percent slopes
CcF	Cataska-Sylco complex, 30 to 95 percent slopes, very rocky
ChF	Cheoah channery loam, 30 to 95 percent slopes, stony
CkF	Chestnut-Cleveland-Rock outcrop complex, 30 to 95 percent slopes, very stony
CmC	Chiltoskie-Heintooga-Horsetrough complex, 8 to 15 percent slopes, very stony
CmD	Chiltoskie-Heintooga complex, 15 to 30 percent slopes, stony
CnF	Clifton clay loam, 50 to 95 percent slopes
CoB	Cotaco silty clay loam, 2 to 8 percent slopes
CuD	Cullasaja-Tuckasegee complex, 15 to 30 percent slopes, very stony
CuE	Cullasaja-Tuckasegee complex, 30 to 50 percent slopes, very stony
CuF	Cullasaja-Rubble land complex, 50 to 95 percent slopes, extremely stony
Cw	Cullowhee-Ela complex, 0 to 2 percent slopes, frequently flooded
Dd	Dellwood-Smokemont-Urban land complex, 0 to 5 percent slopes, occasionally flooded
Dg	Dellwood-Smokemont complex, 0 to 5 percent slopes, frequently flooded
DhB	Dellwood-Wesser complex, 0 to 5 percent slopes, frequently flooded
DtD	Ditney-Unicoi complex, 15 to 30 percent slopes, very rocky
DtF	Ditney-Unicoi complex, 30 to 95 percent slopes, very rocky
EpD	Evard-Cowee complex, 15 to 30 percent slopes, stony, windswept
EpE	Evard-Cowee complex, 30 to 50 percent slopes, stony, windswept
EvD	Evard-Cowee complex, 15 to 30 percent slopes, stony
EvE	Evard-Cowee complex, 30 to 50 percent slopes, stony
EvF	Evard-Cowee complex, 50 to 95 percent slopes, stony
HcE	Heintooga-Chiltoskie complex, 30 to 50 percent slopes, stony
HrF	Heintooga-Rubble land complex, 50 to 95 percent slopes, extremely bouldery
JbD	Junaluska-Brasstown complex, 15 to 30 percent slopes, stony
JbE	Junaluska-Brasstown complex, 30 to 50 percent slopes, stony
JtC	Junaluska-Tsali complex, 8 to 15 percent slopes
JtD	Junaluska-Tsali complex, 15 to 30 percent slopes
JtF	Junaluska-Tsali complex, 30 to 95 percent slopes
LeD	Lauada-Fannin complex, 15 to 30 percent slopes
LeE	Lauada-Fannin complex, 30 to 50 percent slopes
LeF	Lauada-Fannin complex, 50 to 95 percent slopes
LfD	Leatherwood cobbly clay, 15 to 30 percent slopes, stony
LfE	Leatherwood cobbly clay, 30 to 50 percent slopes, stony
LfF	Leatherwood cobbly clay, 50 to 95 percent slopes, stony
LoB	Lonon silty clay loam, 2 to 8 percent slopes
LoC	Lonon silty clay loam, 8 to 15 percent slopes

LoD	Lonon silty clay loam, 15 to 30 percent slopes
LoE	Lonon-Rock outcrop complex, 30 to 50 percent slopes
LrD	Luftee-Anakeesta complex, 15 to 30 percent slopes, very rocky
LrF	Luftee-Anakeesta complex, 30 to 95 percent slopes, very rocky
NtC	Northcove-Maymead-Nowhere complex, 8 to 15 percent slopes, very stony
NtD	Northcove-Maymead complex, 15 to 30 percent slopes, very stony
NtE	Northcove-Maymead complex, 30 to 50 percent slopes, very stony
OcD	Oconaluftee-Guyot-Heintooga complex, 15 to 30 percent slopes, stony
OcF	Oconaluftee-Heintooga-Rubble land complex , 30 to 95 percent slopes, stony
OwC	Oconaluftee-Guyot-Cataloochee complex, 8 to 15 percent slopes, stony, windswept
OwD	Oconaluftee-Guyot-Cataloochee complex, 15 to 30 percent slopes, stony, windswept
OwE	Oconaluftee-Guyot-Cataloochee complex, 30 to 50 percent slopes, stony, windswept
OwF	Oconaluftee-Guyot-Cataloochie complex, 50 to 95 percent slopes, stony, windswept
Po	Potomac very cobbly loamy sand, 0 to 5 percent slopes, extremely bouldery, frequently flooded
Rd	Reddies-Dellwood complex, 0 to 5 percent slopes, frequently flooded
RpF	Rock outcrop-Pullback complex, 30 to 95 percent slopes, stony
RtF	Rock outcrop-Luftee complex, 30 to 95 percent slopes, very stony
RuF	Rock outcrop-Unicoi complex, 30 to 95 percent slopes
Rv	Rosman-Reddies complex, 0 to 5 percent slopes, frequently flooded
Rw	Rosman-Reddies-Urban land complex, 0 to 5 percent slopes, occasionally flooded
RxF	Rubble land-Spivey complex, 50 to 95 percent slopes, extremely bouldery
RZ	Rubble land, 30 to 95 percent slopes
SaD	Saunook loam, 15 to 30 percent slopes, stony
SdC	Saunook-Urbanland complex, 8 to 15 percent slopes, stony
SI	Slide area
SnF	Snowbird loam, 30 to 95 percent slopes, stony
SoD	Soco-Stecoah complex, 15 to 30 percent slopes, stony
SoF	Soco-Stecoah complex, 30 to 95 percent slopes, stony
SpD	Soco-Stecoah complex, 15 to 30 percent slopes, stony, windswept
SpF	Soco-Stecoah complex, 30 to 95 percent slopes, stony, windswept
SsB	Spivey-Santeetlah-Nowhere complex, 2 to 8 percent slopes, very stony
SsC	Spivey-Santeetlah-Nowhere complex, 8 to 15 percent slopes, very stony
SsD	Spivey-Santeetlah complex, 15 to 30 percent slopes, very stony
SsE	Spivey-Santeetlah complex, 30 to 50 percent slopes, very stony
StB	Statler loam, 0 to 5 percent slopes
StC	Statler loam, 5 to 15 percent slopes
TaC	Tanasee-Balsam complex, 5 to 15 percent slopes, stony
TaD	Tanasee-Balsam complex, 15 to 30 percent slopes, stony
ThB	Thurmont-Dillard complex, 2 to 8 percent slopes, stony
ThC	Thurmont loam, 8 to 15 percent slopes, stony
To	Toxaway silty clay loam, 0 to 2 percent slopes, occasionally flooded
TuC	Tuckasegee-Cullasaja complex, 8 to 15 percent slopes, stony
Ud	Udorthents-loamy
W	Water
WaC	Wayah sandy loam, 5 to 15 percent slopes, stony, windswept
WaD	Wayah sandy loam, 15 to 30 percent slopes, stony, windswept
WaF	Wayah sandy loam, 30 to 95 percent slopes, stony, windswept
WeD	Wayah sandy loam, 15 to 30 percent slopes, stony
WeF	Wayah sandy loam, 30 to 95 percent slopes, stony

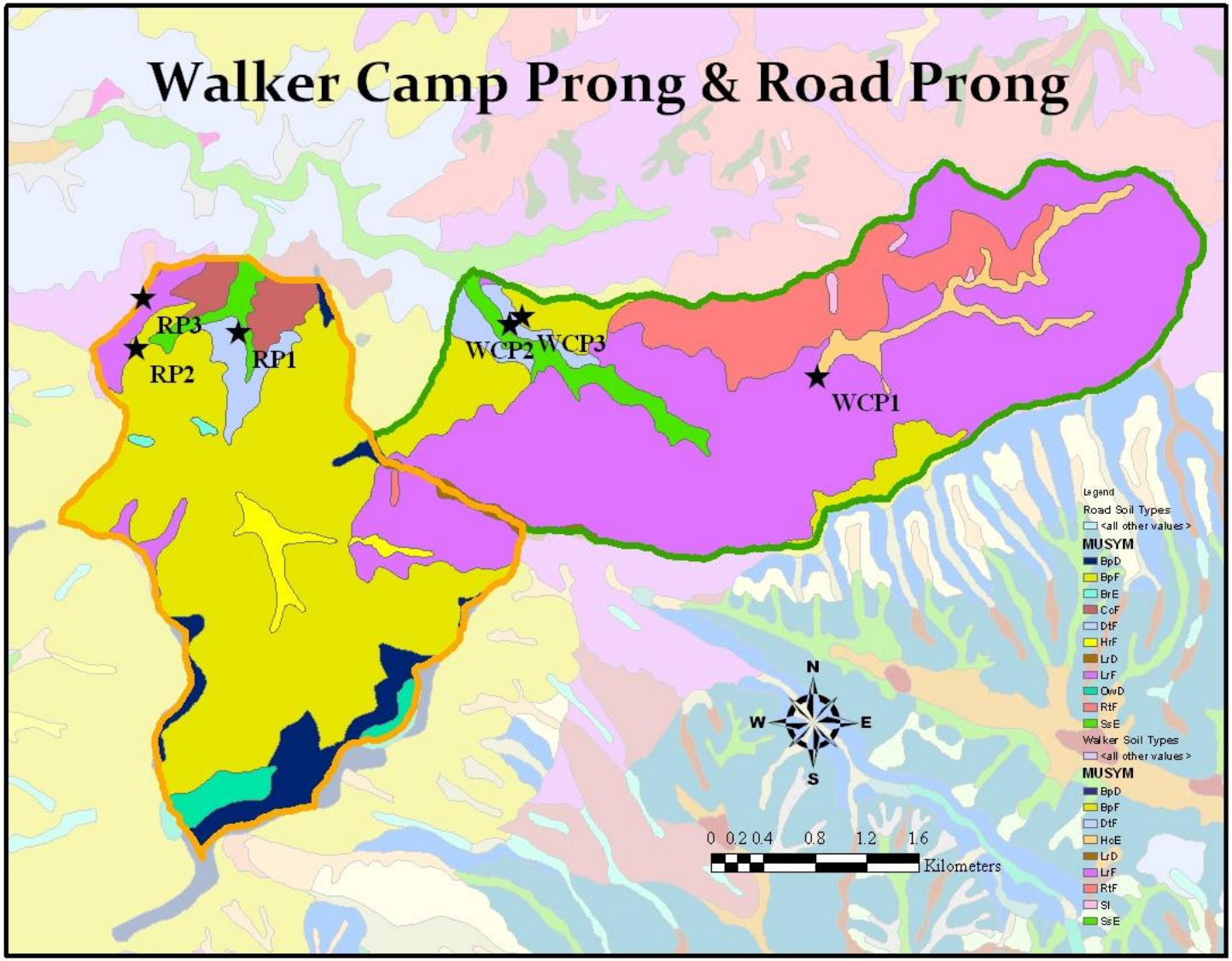
A4. Soil Taxonomic Classification for GRSM

Soil Name	Taxonomic Classification
Alarka	Fine-loamy over sandy or sandy-skeletal, mixed, active, mesic Aeric Epiaquults
Allegheny	Fine-loamy, mixed, semiactive, mesic Typic Hapludults
Anakeesta	Loamy-skeletal, isotic, frigid Humic Dystrudepts
Balsam	Loamy-skeletal, isotic, frigid Humic Dystrudepts
Biltmore	Mixed, mesic Typic Udipsamments
Brasstown	Fine-loamy, mixed, subactive, mesic Typic Hapludults
Breakneck	Fine-loamy, isotic, frigid Humic Dystrudepts
Burton	Fine-loamy, isotic, frigid Humic Dystrudepts
Cades	Fine-loamy, mixed, semiactive, mesic Typic Hapludults
Cataloochee	Fine-loamy, isotic, frigid Humic Dystrudepts
Cataska	Loamy-skeletal, mixed, semiactive, mesic, shallow Typic Dystrudepts
Cheoah	Fine-loamy, isotic, mesic Humic Dystrudepts
Chestnut	Coarse-loamy, mixed, active, mesic Typic Dystrudepts
Chiltoskie	Fine-loamy, isotic, frigid Typic Dystrudepts
Cleveland	Loamy, mixed, active, mesic Lithic Dystrudepts
Clifton	Fine, mixed, semiactive, mesic Typic Hapludults
Clingman	Dysic, frigid Lithic Udifolists
Cotaco	Fine-loamy, mixed, semiactive, mesic Aquic Hapludults
Cowee	Fine-loamy, parasesquic, mesic Typic Hapludults
Craggey	Loamy, isotic, frigid Humic Lithic Dystrudepts
Cullasaja	Loamy-skeletal, isotic, mesic Humic Dystrudepts
Cullowhee	Coarse-loamy over sandy or sandy-skeletal, mixed, superactive, mesic Fluvaquentic Dystrudepts
Dellwood	Sandy-skeletal, mixed, mesic Oxyaquic Dystrudepts
Dillard	Fine-loamy, mixed, semiactive, mesic Aquic Hapludults
Ditney	Coarse-loamy, mixed, semiactive, mesic Typic Dystrudepts
Ela	Coarse-loamy, siliceous, superactive, acid, mesic Fluvaquentic Humaquepts
Evard	Fine-loamy, parasesquic, mesic Typic Hapludults
Fannin	Fine-loamy, paramicaceous, mesic Typic Hapludults
Guyot	Fine-loamy, isotic, frigid Humic Dystrudepts
Heintooga	Loamy-skeletal, isotic, frigid Humic Dystrudepts
Horsetrough	Sandy-skeletal, isotic, frigid Typic Humaquepts
Junaluska	Fine-loamy, mixed, subactive, mesic Typic Hapludults
Lauada	Fine-loamy, micaceous, mesic Typic Hapludults
Leatherwood	Fine, mixed, semiactive, mesic Humic Dystrudepts
Lonon*	Fine, mixed, semiactive, mesic Typic Hapludults
Luftee	Loamy-skeletal, isotic, frigid Humic Dystrudepts
Maymead	Coarse-loamy, mixed, semiactive, mesic Typic Dystrudepts
Northcove	Loamy-skeletal, mixed, semiactive, mesic Typic Dystrudepts
Nowhere	Loamy-skeletal, isotic, acid, mesic Typic Humaquepts
Oconaluftee	Fine-loamy, isotic, frigid Humic Dystrudepts
Pinnacle	Dysic, frigid Typic Udifolists
Potomac	Sandy-skeletal, mixed, mesic Typic Udifluvents
Pullback	Loamy, isotic, frigid Humic Lithic Dystrudepts
Reddies	Coarse-loamy over sandy or sandy-skeletal, mixed, superactive, mesic Oxyaquic Dystrudepts
Rosman	Coarse-loamy, mixed, superactive, mesic Fluventic Humic Dystrudepts

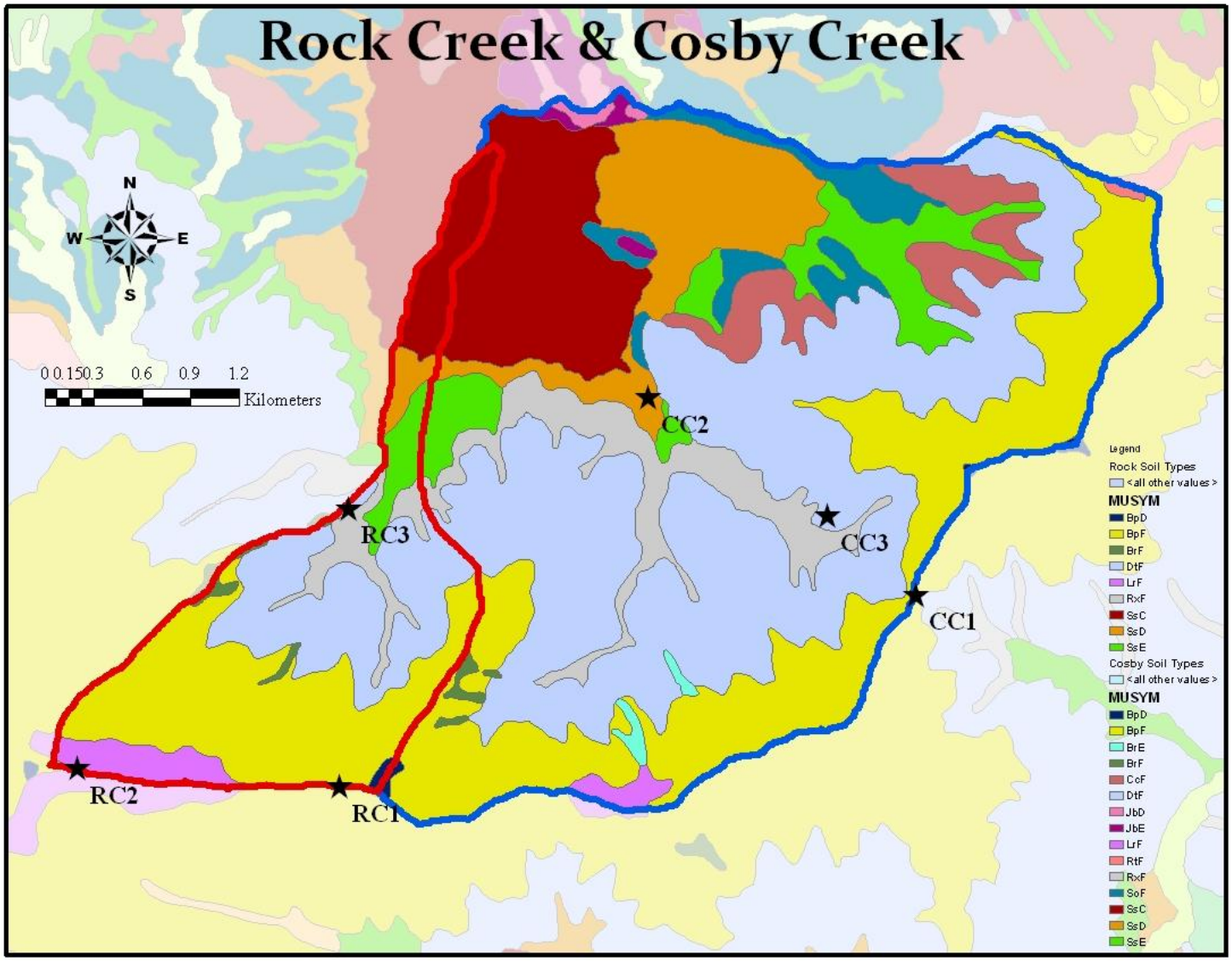
Santeetlah	Fine-loamy, isotic, mesic Humic Dystrudepts
Saunook	Fine-loamy, mixed, superactive, mesic Humic Hapludults
Smokemont	Sandy-skeletal, mixed, mesic Fluventic Humic Dystrudepts
Snowbird	Fine-loamy, mixed, active, mesic Humic Hapludults
Soco	Coarse-loamy, mixed, active, mesic Typic Dystrudepts
Spivey	Loamy-skeletal, isotic, mesic Humic Dystrudepts
Statler	Fine-loamy, mixed, active, mesic Humic Hapludults
Stecoah	Coarse-loamy, mixed, active, mesic Typic Dystrudepts
Sylco	Loamy-skeletal, mixed, active, mesic Typic Dystrudepts
Tanasee	Fine-loamy, isotic, frigid Humic Dystrudepts
Thurmont	Fine-loamy, mixed, active, mesic Oxyaquic Hapludults
Toxaway*	Fine-silty, mixed, superactive, nonacid, mesic Cumulic Humaquepts
Tsali	Loamy, mixed, subactive, mesic, shallow Typic Hapludults
Tuckasegee	Fine-loamy, isotic, mesic Humic Dystrudepts
Udorthents	Udorthents
Unicoi	Loamy-skeletal, mixed, semiactive, mesic Lithic Dystrudepts
Wayah	Fine-loamy, isotic, frigid Humic Dystrudepts
Wesser	Sandy-skeletal, mixed, mesic Humaqueptic Fluvaquents
Whiteside	Fine-loamy, mixed, active, mesic Aquic Hapludults



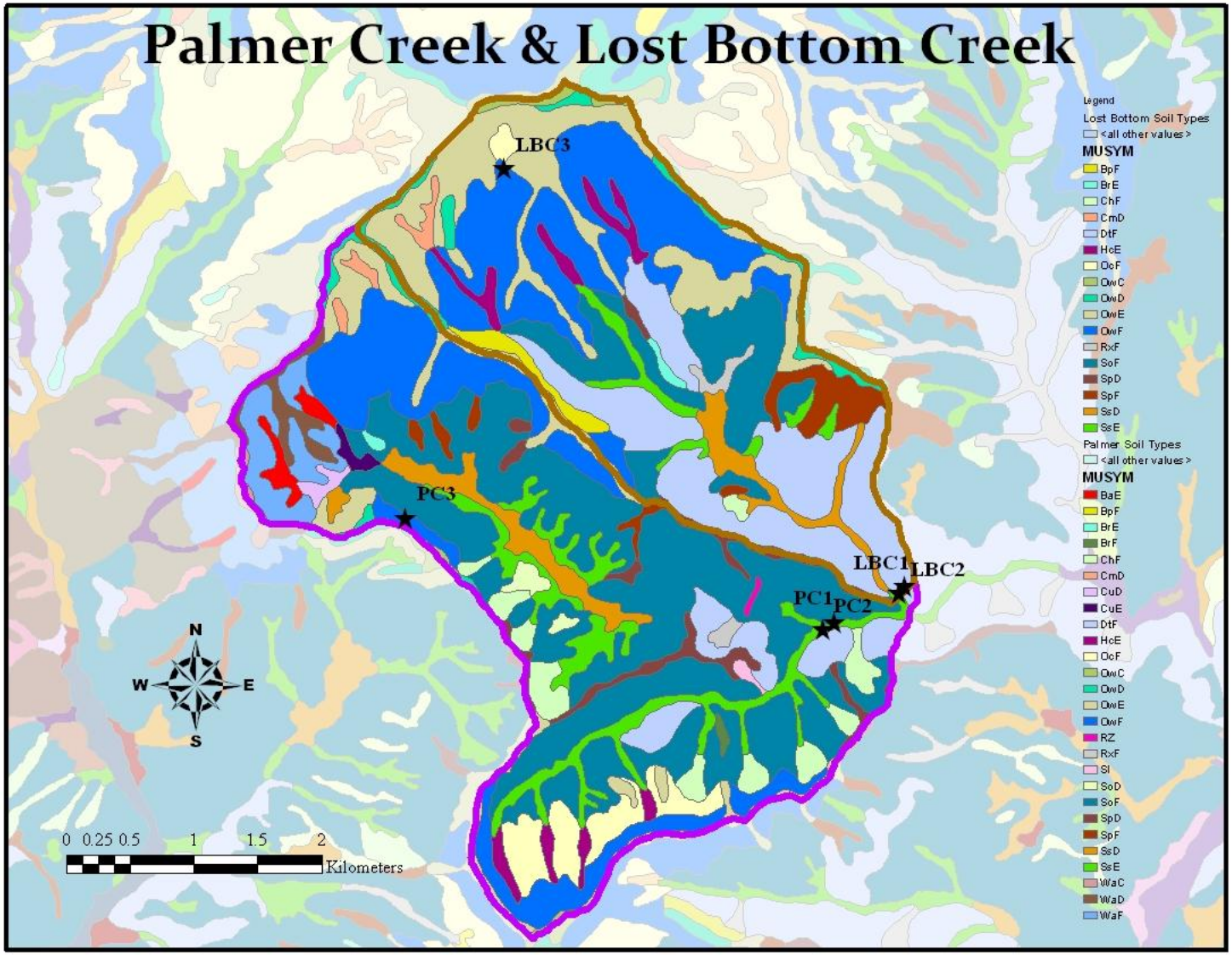
A5. Soil types and site selection for Newt Prong and Jakes Creek.



A6. Soil types and site selection for Road Prong and Walker Camp Prong.



A7. Soil types and site selection for Rock Creek and Cosby Creek.



A8. Soil types and site selection for Palmer Creek and Lost Bottom Creek.

A9. Pearson (pairwise) correlation of chemical parameters only. Chemical property values from Walker Camp Prong are NOT included. Bold indicates significant relationships.

Variable	by Variable	A Horizon Correlation	Count	Lower 95%	Upper 95%	Signif Prob	B/C Horizon Correlation	Count	Lower 95%	Upper 95%	Signif Prob
pH_{H2O}	Al:Ca	0.0855	22	-0.3486	0.4895	0.705	**0.5715**	**22**	**0.1975**	**0.8003**	**0.0055**
pH_{CaCl2}	Al:Ca	0.0136	22	-0.4104	0.4327	0.9522	**0.493**	**22**	**0.0901**	**0.7572**	**0.0197**
pH_{CaCl2}	pH_{H2O}	**0.892**	**22**	**0.7539**	**0.9546**	**<.0001**	**0.8508**	**22**	**0.6692**	**0.9365**	**<.0001**
OM	Al:Ca	0.3337	22	-0.1023	0.6622	0.1291	0.1499	22	-0.2901	0.5375	0.5056
OM	pH_{H2O}	**-0.7381**	**22**	**-0.8845**	**-0.4595**	**<.0001**	-0.0423	22	-0.4558	0.3862	0.8516
OM	pH_{CaCl2}	**-0.8542**	**22**	**-0.938**	**-0.6761**	**<.0001**	0.1846	22	-0.257	0.5624	0.4109
TON	Al:Ca	0.4114	22	-0.0123	0.7099	0.0571	0.3078	22	-0.1307	0.6457	0.1634
TON	pH_{H2O}	**-0.7476**	**22**	**-0.889**	**-0.476**	**<.0001**	0.029	22	-0.3975	0.4452	0.8981
TON	pH_{CaCl2}	**-0.8197**	**22**	**-0.9225**	**-0.6082**	**<.0001**	0.2868	22	-0.1533	0.632	0.1956
TON	OM	**0.9544**	**22**	**0.8915**	**0.9812**	**<.0001**	**0.7655**	**22**	**0.5077**	**0.8974**	**<.0001**
Na^+	Al:Ca	-0.0743	22	-0.4808	0.3585	0.7424	0.0145	22	-0.4096	0.4335	0.9489
Na^+	pH_{H2O}	**-0.5958**	**22**	**-0.8131**	**-0.2326**	**0.0034**	-0.243	22	-0.6028	0.199	0.2759
Na^+	pH_{CaCl2}	**-0.652**	**22**	**-0.8421**	**-0.3177**	**0.001**	-0.1008	22	-0.5011	0.3351	0.6554
Na^+	OM	**0.7204**	**22**	**0.4291**	**0.8759**	**0.0002**	0.1428	22	-0.2967	0.5324	0.5261
Na^+	TON	**0.5698**	**22**	**0.1951**	**0.7994**	**0.0056**	0.3026	22	-0.1364	0.6423	0.171
K^+	Al:Ca	0.3177	22	-0.12	0.652	0.1496	0.0914	22	-0.3434	0.494	0.6857
K^+	pH_{H2O}	-0.402	22	-0.7042	0.0236	0.0637	0.2566	22	-0.185	0.612	0.249
K^+	pH_{CaCl2}	**-0.5976**	**22**	**-0.8141**	**-0.2352**	**0.0033**	0.1789	22	-0.2625	0.5584	0.4256
K^+	OM	**0.7472**	**22**	**0.4753**	**0.8888**	**<.0001**	**0.5887**	**22**	**0.2222**	**0.8094**	**0.0039**
K^+	TON	**0.7523**	**22**	**0.4844**	**0.8913**	**<.0001**	**0.493**	**22**	**0.0902**	**0.7572**	**0.0197**
K^+	Na^+	0.3419	22	-0.0932	0.6673	0.1194	-0.1756	22	-0.5561	0.2656	0.4343
Mg^{2+}	Al:Ca	**0.453**	**22**	**0.0388**	**0.7344**	**0.0342**	**0.5936**	**22**	**0.2294**	**0.812**	**0.0036**
Mg^{2+}	pH_{H2O}	-0.3856	22	-0.6943	0.043	0.0764	0.2799	22	-0.1606	0.6275	0.207

Mg^{2+}	pH_{CaCl2}	**-0.5696**	**22**	**-0.7993**	**-0.1948**	**0.0057**	0.2339	22	-0.2083	0.5967	0.2948
Mg^{2+}	OM	**0.748**	**22**	**0.4767**	**0.8892**	**<.0001**	**0.5901**	**22**	**0.2243**	**0.8102**	**0.0038**
Mg^{2+}	TON	**0.7463**	**22**	**0.4738**	**0.8884**	**<.0001**	**0.6973**	**22**	**0.3904**	**0.8647**	**0.0003**
Mg^{2+}	Na^{+}	0.2762	22	-0.1645	0.625	0.2134	0.0427	22	-0.3858	0.4561	0.8503
Mg^{2+}	K^{+}	**0.8613**	**22**	**0.6904**	**0.9411**	**<.0001**	**0.6974**	**22**	**0.3907**	**0.8648**	**0.0003**
Ca^{2+}	Al:Ca	**0.892**	**22**	**0.7538**	**0.9546**	**<.0001**	**0.8916**	**22**	**0.753**	**0.9544**	**<.0001**
Ca^{2+}	pH_{H2O}	-0.1457	22	-0.5345	0.2939	0.5176	**0.4412**	**22**	**0.0241**	**0.7275**	**0.0398**
Ca^{2+}	pH_{CaCl2}	-0.233	22	-0.596	0.2092	0.2968	0.3698	22	-0.0613	0.6847	0.0902
Ca^{2+}	OM	**0.5221**	**22**	**0.1289**	**0.7735**	**0.0127**	0.3362	22	-0.0995	0.6638	0.126
Ca^{2+}	TON	**0.5917**	**22**	**0.2266**	**0.811**	**0.0037**	**0.4857**	**22**	**0.0806**	**0.7531**	**0.0219**
Ca^{2+}	Na^{+}	-0.0415	22	-0.4551	0.3869	0.8545	-0.1104	22	-0.5083	0.3264	0.6248
Ca^{2+}	K^{+}	**0.5825**	**22**	**0.2133**	**0.8061**	**0.0044**	0.339	22	-0.0964	0.6655	0.1228
Ca^{2+}	Mg^{2+}	**0.6783**	**22**	**0.3594**	**0.8553**	**0.0005**	**0.8218**	**22**	**0.6123**	**0.9234**	**<.0001**
EBC	Al:Ca	**0.7933**	**22**	**0.5586**	**0.9104**	**<.0001**	**0.7074**	**22**	**0.4073**	**0.8697**	**0.0002**
EBC	pH_{H2O}	-0.262	22	-0.6156	0.1794	0.2388	0.4159	22	-0.0069	0.7126	0.0542
EBC	pH_{CaCl2}	-0.3959	22	-0.7006	0.0308	0.0682	0.3378	22	-0.0977	0.6647	0.1242
EBC	OM	**0.6682**	**22**	**0.3434**	**0.8503**	**0.0007**	**0.5373**	**22**	**0.1496**	**0.7818**	**0.0099**
EBC	TON	**0.7153**	**22**	**0.4205**	**0.8735**	**0.0002**	**0.6219**	**22**	**0.2715**	**0.8268**	**0.002**
EBC	Na^{+}	0.0995	22	-0.3362	0.5002	0.6594	-0.1023	22	-0.5023	0.3337	0.6505
EBC	K^{+}	**0.7615**	**22**	**0.5006**	**0.8956**	**<.0001**	**0.698**	**22**	**0.3917**	**0.865**	**0.0003**
EBC	Mg^{2+}	**0.8522**	**22**	**0.672**	**0.9371**	**<.0001**	**0.9591**	**22**	**0.9023**	**0.9831**	**<.0001**
EBC	Ca^{2+}	**0.9601**	**22**	**0.9046**	**0.9836**	**<.0001**	**0.9055**	**22**	**0.7827**	**0.9604**	**<.0001**
Al	Al:Ca	**-0.7538**	**22**	**-0.892**	**-0.487**	**<.0001**	**-0.6535**	**22**	**-0.8429**	**-0.3201**	**0.001**
Al	pH_{H2O}	-0.2337	22	-0.5965	0.2084	0.2952	**-0.6808**	**22**	**-0.8566**	**-0.3635**	**0.0005**
Al	pH_{CaCl2}	-0.2025	22	-0.575	0.2396	0.3662	**-0.7126**	**22**	**-0.8722**	**-0.4159**	**0.0002**
Al	OM	-0.1451	22	-0.534	0.2946	0.5195	0.0726	22	-0.36	0.4795	0.7481
Al	TON	-0.1216	22	-0.5167	0.3162	0.5899	-0.1733	22	-0.5544	0.2679	0.4407

Al	Na^+	-0.0348	22	-0.4498	0.3926	0.878	-0.1488	22	-0.5368	0.291	0.5086
Al	K^+	-0.1578	22	-0.5433	0.2826	0.4831	0.0401	22	-0.3881	0.454	0.8593
Al	Mg^{2+}	-0.3775	22	-0.6894	0.0524	0.0832	-0.1861	22	-0.5635	0.2556	0.407
Al	Ca^{2+}	**-0.6194**	**22**	**-0.8255**	**-0.2677**	**0.0021**	-0.4016	22	-0.704	0.024	0.0639
Al	EBC	**-0.5631**	**22**	**-0.7958**	**-0.1856**	**0.0064**	-0.2762	22	-0.625	0.1646	0.2134
NO_3^-	Al:Ca	0.1321	22	-0.3066	0.5245	0.5578	0.2949	22	-0.1447	0.6373	0.1827
NO_3^-	pH_{H2O}	-0.1763	22	-0.5565	0.265	0.4326	-0.0993	22	-0.5	0.3364	0.6602
NO_3^-	pH_{CaCl2}	0.2089	22	-0.2332	0.5795	0.3507	0.1996	22	-0.2424	0.573	0.3731
NO_3^-	OM	-0.1613	22	-0.5458	0.2793	0.4734	**0.4416**	**22**	**0.0245**	**0.7277**	**0.0396**
NO_3^-	TON	-0.0293	22	-0.4454	0.3972	0.8969	**0.7718**	**22**	**0.5192**	**0.9004**	**<.0001**
NO_3^-	Na^+	-0.269	22	-0.6203	0.1721	0.226	**0.5438**	**22**	**0.1585**	**0.7853**	**0.0089**
NO_3^-	K^+	-0.3679	22	-0.6835	0.0636	0.0921	0.0208	22	-0.4043	0.4386	0.9267
NO_3^-	Mg^{2+}	-0.2375	22	-0.5991	0.2046	0.2873	0.4015	22	-0.0242	0.7039	0.064
NO_3^-	Ca^{2+}	0.1141	22	-0.323	0.5111	0.6131	0.3793	22	-0.0504	0.6905	0.0817
NO_3^-	EBC	-0.0261	22	-0.4429	0.3999	0.9081	0.3353	22	-0.1005	0.6632	0.1271
NO_3^-	Al	-0.0918	22	-0.4943	0.3431	0.6844	-0.2197	22	-0.5869	0.2225	0.3259
NH_4^+	Al:Ca	0.406	22	-0.0188	0.7067	0.0608	0.1029	22	-0.3331	0.5027	0.6485
NH_4^+	pH_{H2O}	-0.1668	22	-0.5497	0.2741	0.4582	0.0283	22	-0.3981	0.4446	0.9005
NH_4^+	pH_{CaCl2}	-0.3811	22	-0.6916	0.0483	0.0801	-0.1554	22	-0.5415	0.2849	0.4898
NH_4^+	OM	**0.5017**	**22**	**0.1016**	**0.7621**	**0.0174**	**0.4685**	**22**	**0.0585**	**0.7433**	**0.0278**
NH_4^+	TON	**0.5069**	**22**	**0.1084**	**0.765**	**0.0161**	0.1705	22	-0.2706	0.5524	0.4481
NH_4^+	Na^+	0.0483	22	-0.3811	0.4605	0.8311	-0.2535	22	-0.6099	0.1883	0.2551
NH_4^+	K^+	**0.6791**	**22**	**0.3607**	**0.8557**	**0.0005**	**0.547**	**22**	**0.1629**	**0.7871**	**0.0084**
NH_4^+	Mg^{2+}	**0.6572**	**22**	**0.3259**	**0.8447**	**0.0009**	**0.4997**	**22**	**0.099**	**0.761**	**0.0179**
NH_4^+	Ca^{2+}	**0.6707**	**22**	**0.3473**	**0.8515**	**0.0006**	0.3243	22	-0.1127	0.6562	0.1409
NH_4^+	EBC	**0.7303**	**22**	**0.4461**	**0.8807**	**0.0001**	**0.4896**	**22**	**0.0856**	**0.7553**	**0.0207**

NH_4^+	Al	-0.0911	22	-0.4937	0.3437	0.6869	0.375	22	-0.0554	0.6879	0.0855
NH_4^+	NO_3^-	-0.226	22	-0.5913	0.2162	0.3119	-0.1923	22	-0.5679	0.2495	0.3912
SO_4^{2-}	Al:Ca	0.3763	22	-0.0539	0.6886	0.0844	0.1336	22	-0.3052	0.5256	0.5533
SO_4^{2-}	pH_{H2O}	-0.3783	22	-0.6899	0.0516	0.0826	0.0564	22	-0.3741	0.4669	0.8032
SO_4^{2-}	pH_{CaCl2}	**-0.5496**	**22**	**-0.7885**	**-0.1666**	**0.0081**	0.2036	22	-0.2384	0.5758	0.3633
SO_4^{2-}	OM	**0.823**	**22**	**0.6147**	**0.924**	**<.0001**	**0.6643**	**22**	**0.3371**	**0.8483**	**0.0007**
SO_4^{2-}	TON	**0.7294**	**22**	**0.4444**	**0.8803**	**0.0001**	0.3464	22	-0.0881	0.6701	0.1143
SO_4^{2-}	Na^+	**0.5526**	**22**	**0.1708**	**0.7901**	**0.0077**	-0.1312	22	-0.5238	0.3075	0.5607
SO_4^{2-}	K^+	**0.7456**	**22**	**0.4725**	**0.8881**	**<.0001**	**0.5121**	**22**	**0.1154**	**0.7679**	**0.0148**
SO_4^{2-}	Mg^{2+}	**0.7625**	**22**	**0.5024**	**0.896**	**<.0001**	0.4128	22	-0.0107	0.7107	0.0562
SO_4^{2-}	Ca^{2+}	**0.5552**	**22**	**0.1744**	**0.7915**	**0.0073**	0.2323	22	-0.2098	0.5956	0.2982
SO_4^{2-}	EBC	**0.6926**	**22**	**0.3827**	**0.8624**	**0.0004**	0.4047	22	-0.0204	0.7058	0.0618
SO_4^{2-}	Al	-0.3041	22	-0.6433	0.1347	0.1688	0.0479	22	-0.3814	0.4602	0.8325
SO_4^{2-}	NO_3^-	-0.2525	22	-0.6092	0.1893	0.2569	0.0168	22	-0.4077	0.4354	0.9407
SO_4^{2-}	NH_4^+	**0.6375**	**22**	**0.2953**	**0.8348**	**0.0014**	**0.5494**	**22**	**0.1663**	**0.7884**	**0.0081**
TSO_4	Al:Ca	0.2934	22	-0.1463	0.6363	0.1851	0.1464	22	-0.2934	0.535	0.5157
TSO_4	pH_{H2O}	0.4143	22	-0.0089	0.7116	0.0553	0.3412	22	-0.0939	0.6669	0.1201
TSO_4	pH_{CaCl2}	**0.4411**	**22**	**0.024**	**0.7275**	**0.0399**	**0.642**	**22**	**0.3022**	**0.837**	**0.0013**
TSO_4	OM	-0.0648	22	-0.4735	0.3668	0.7744	0.2295	22	-0.2126	0.5937	0.3041
TSO_4	TON	-0.0759	22	-0.4821	0.3571	0.7371	0.2899	22	-0.1501	0.634	0.1907
TSO_4	Na^+	-0.0978	22	-0.4988	0.3378	0.6651	-0.255	22	-0.6109	0.1867	0.2521
TSO_4	K^+	-0.0473	22	-0.4597	0.382	0.8346	0.0586	22	-0.3722	0.4686	0.7957
TSO_4	Mg^{2+}	-0.0229	22	-0.4402	0.4026	0.9196	-0.0449	22	-0.4578	0.384	0.8428
TSO_4	Ca^{2+}	0.1287	22	-0.3098	0.522	0.5683	0.0285	22	-0.3979	0.4447	0.9
TSO_4	EBC	0.0791	22	-0.3543	0.4846	0.7263	0.024	22	-0.4017	0.4411	0.9156
TSO_4	Al	-0.2687	22	-0.62	0.1725	0.2267	**-0.4515**	**22**	**-0.7335**	**-0.0369**	**0.0349**
TSO_4	NO_3^-	0.1334	22	-0.3054	0.5254	0.554	0.1418	22	-0.2976	0.5317	0.5289

TSO_4	NH_4^+	0.0207	22	-0.4044	0.4385	0.9271	-0.1801	22	-0.5593	0.2613	0.4225
TSO_4	SO_4^{2-}	0.3281	22	-0.1086	0.6586	0.1361	0.3948	22	-0.0321	0.6999	0.069
EA	Al:Ca	-0.0712	22	-0.4784	0.3613	0.753	**-0.5167**	**22**	**-0.7705**	**-0.1216**	**0.0138**
EA	pH_{H2O}	**-0.8002**	**22**	**-0.9136**	**-0.5713**	**<.0001**	**-0.7113**	**22**	**-0.8715**	**-0.4137**	**0.0002**
EA	pH_{CaCl2}	**-0.9197**	**22**	**-0.9665**	**-0.8135**	**<.0001**	**-0.7353**	**22**	**-0.8831**	**-0.4546**	**<.0001**
EA	OM	**0.8473**	**22**	**0.6622**	**0.9349**	**<.0001**	0.1799	22	-0.2616	0.5591	0.4231
EA	TON	**0.8258**	**22**	**0.6201**	**0.9253**	**<.0001**	-0.1121	22	-0.5096	0.3249	0.6194
EA	Na^+	**0.6442**	**22**	**0.3057**	**0.8382**	**0.0012**	-0.0977	22	-0.4988	0.3378	0.6654
EA	K^+	**0.6301**	**22**	**0.284**	**0.831**	**0.0017**	0.0374	22	-0.3904	0.4519	0.8688
EA	Mg^{2+}	**0.5151**	**22**	**0.1195**	**0.7696**	**0.0142**	-0.0878	22	-0.4912	0.3467	0.6978
EA	Ca^{2+}	0.1669	22	-0.274	0.5498	0.4578	-0.2744	22	-0.6238	0.1665	0.2165
EA	EBC	0.3371	22	-0.0986	0.6643	0.125	-0.177	22	-0.557	0.2643	0.4307
EA	Al	0.3801	22	-0.0495	0.691	0.081	**0.9645**	**22**	**0.915**	**0.9854**	**<.0001**
EA	NO_3^-	-0.2419	22	-0.6021	0.2002	0.2782	-0.1513	22	-0.5386	0.2887	0.5014
EA	NH_4^+	**0.4332**	**22**	**0.0142**	**0.7228**	**0.044**	**0.4559**	**22**	**0.0424**	**0.736**	**0.033**
EA	SO_4^{2-}	**0.5818**	**22**	**0.2123**	**0.8058**	**0.0045**	0.1435	22	-0.296	0.5329	0.5241
EA	TSO_4	-0.2653	22	-0.6178	0.176	0.2328	**-0.4798**	**22**	**-0.7498**	**-0.073**	**0.0238**
ECEC	Al:Ca	0.2605	22	-0.181	0.6146	0.2417	**-0.4574**	**22**	**-0.7369**	**-0.0444**	**0.0323**
ECEC	pH_{H2O}	**-0.7384**	**22**	**-0.8846**	**-0.46**	**<.0001**	**-0.6814**	**22**	**-0.8569**	**-0.3645**	**0.0005**
ECEC	pH_{CaCl2}	**-0.8865**	**22**	**-0.9522**	**-0.7423**	**<.0001**	**-0.713**	**22**	**-0.8723**	**-0.4166**	**0.0002**
ECEC	OM	**0.9379**	**22**	**0.854**	**0.9743**	**<.0001**	0.2319	22	-0.2103	0.5953	0.2991
ECEC	TON	**0.9397**	**22**	**0.8581**	**0.975**	**<.0001**	-0.0558	22	-0.4665	0.3746	0.8051
ECEC	Na^+	**0.55**	**22**	**0.1671**	**0.7887**	**0.008**	-0.1084	22	-0.5068	0.3282	0.6312
ECEC	K^+	**0.8032**	**22**	**0.577**	**0.915**	**<.0001**	0.1026	22	-0.3335	0.5024	0.6497
ECEC	Mg^{2+}	**0.7483**	**22**	**0.4773**	**0.8893**	**<.0001**	0.0001	22	-0.4215	0.4217	0.9997
ECEC	Ca^{2+}	**0.5156**	**22**	**0.1202**	**0.7699**	**0.014**	-0.1938	22	-0.5689	0.2481	0.3874
ECEC	EBC	**0.6663**	**22**	**0.3403**	**0.8493**	**0.0007**	-0.0864	22	-0.4902	0.3478	0.7021
ECEC	Al	0.0761	22	-0.357	0.4822	0.7364	**0.9507**	**22**	**0.8831**	**0.9797**	**<.0001**

ECEC	NO_3^-	-0.202	22	-0.5747	0.2401	0.3674	-0.1221	22	-0.5171	0.3158	0.5883
ECEC	NH_4^+	**0.6348**	**22**	**0.2911**	**0.8334**	**0.0015**	**0.5068**	**22**	**0.1084**	**0.765**	**0.0161**
ECEC	SO_4^{2-}	**0.7374**	**22**	**0.4583**	**0.8841**	**<.0001**	0.1828	22	-0.2588	0.5611	0.4156
ECEC	TSO_4	-0.1785	22	-0.5581	0.2629	0.4268	**-0.4835**	**22**	**-0.7518**	**-0.0777**	**0.0226**
ECEC	EA	**0.9266**	**22**	**0.8288**	**0.9695**	**<.0001**	**0.9958**	**22**	**0.9898**	**0.9983**	**<.0001**
BS	Al:Ca	**0.8261**	**22**	**0.6207**	**0.9254**	**<.0001**	**0.9231**	**22**	**0.8211**	**0.968**	**<.0001**
BS	pH_{H2O}	0.3517	22	-0.0821	0.6735	0.1085	**0.6805**	**22**	**0.3631**	**0.8564**	**0.0005**
BS	pH_{CaCl2}	0.2522	22	-0.1896	0.609	0.2576	**0.6012**	**22**	**0.2406**	**0.816**	**0.0031**
BS	OM	0.139	22	-0.3002	0.5296	0.5373	0.2645	22	-0.1769	0.6173	0.2343
BS	TON	0.1521	22	-0.288	0.5391	0.4992	**0.4657**	**22**	**0.0548**	**0.7417**	**0.029**
BS	Na^+	-0.1523	22	-0.5393	0.2878	0.4986	-0.0495	22	-0.4615	0.3801	0.8269
BS	K^+	0.323	22	-0.1142	0.6553	0.1426	0.3944	22	-0.0326	0.6997	0.0693
BS	Mg^{2+}	**0.4762**	**22**	**0.0684**	**0.7477**	**0.0251**	**0.7449**	**22**	**0.4713**	**0.8877**	**<.0001**
BS	Ca^{2+}	**0.7612**	**22**	**0.5001**	**0.8954**	**<.0001**	**0.9024**	**22**	**0.7759**	**0.9591**	**<.0001**
BS	EBC	**0.7052**	**22**	**0.4035**	**0.8685**	**0.0002**	**0.8494**	**22**	**0.6664**	**0.9358**	**<.0001**
BS	Al	**-0.8791**	**22**	**-0.949**	**-0.7269**	**<.0001**	**-0.6841**	**22**	**-0.8582**	**-0.369**	**0.0004**
BS	NO_3^-	0.0301	22	-0.3965	0.4461	0.8941	0.3028	22	-0.1362	0.6424	0.1708
BS	NH_4^+	0.3326	22	-0.1036	0.6614	0.1305	0.1557	22	-0.2846	0.5418	0.489
BS	SO_4^{2-}	0.3903	22	-0.0375	0.6972	0.0725	0.2027	22	-0.2393	0.5752	0.3655
BS	TSO_4	0.4122	22	-0.0113	0.7104	0.0566	0.2238	22	-0.2185	0.5897	0.3168
BS	EA	-0.3189	22	-0.6527	0.1187	0.1481	**-0.5959**	**22**	**-0.8132**	**-0.2328**	**0.0034**
BS	ECEC	0.0291	22	-0.3974	0.4452	0.8977	**-0.5245**	**22**	**-0.7748**	**-0.132**	**0.0122**

VITA

Mary Ann E. Grell was born the youngest of nine children to Ronald A. Grell and Julia C. Pustulka on November 1, 1973 in Buffalo, New York. She attended Good Shepherd, a Catholic elementary school in Pendleton, New York from 1978-1987, followed by Villa Maria Academy, a Catholic all female high school in Buffalo, New York from 1987-1991. She went on to attend the State University of New York at Alfred where she received an Associate degree in Arts in May of 1993. She then worked in retail for two years before deciding to go back to school at the State University of New York at Delhi. There she received an Associate degree in Applied Science with a concentration in Veterinary Science in December of 1996. In February of 1997, Mary Ann relocated to Knoxville, Tennessee where she worked as a Licensed Veterinary Medical Technician for eight years. During that time she was involved in the National Veterinary Technician Association, the Tennessee Veterinary Technician Association and served a two year term on the Tennessee Board of Veterinary Medical Examiners as the sole veterinary technician representative. Once again in August of 2005, Mary Ann returned to school at the University of Tennessee, Knoxville, where she obtained a Bachelor of Science degree in Civil Engineering in December of 2008. While completing this undergraduate degree, she was initiated into Chi Epsilon Honor Society for Civil Engineers and was active in the student chapter of the American Society of Civil Engineers. She also worked as a co-op student for a local engineering firm that concentrated in the design of municipal water and wastewater systems. Following graduation, Mary Ann received her certification as an Engineering Intern and accepted a graduate research assistantship at the University of Tennessee, Knoxville, in the Department of Civil and Environmental Engineering in January of 2009. During graduate school, her main responsibilities were to assist in teaching the undergraduate hydraulics lab and carry out soil chemistry and water quality research in the Great Smoky Mountains National Park. In August of 2010, she accepted an appointment to the Research Participation Program at the U.S. Environmental Protection Agency and will serve her appointment at the Tennessee Department of Environment and Conservation. Mary Ann graduated in December of 2010 with a Master of Science degree in Environmental Engineering concentrating in Water Resources.